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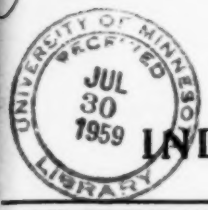

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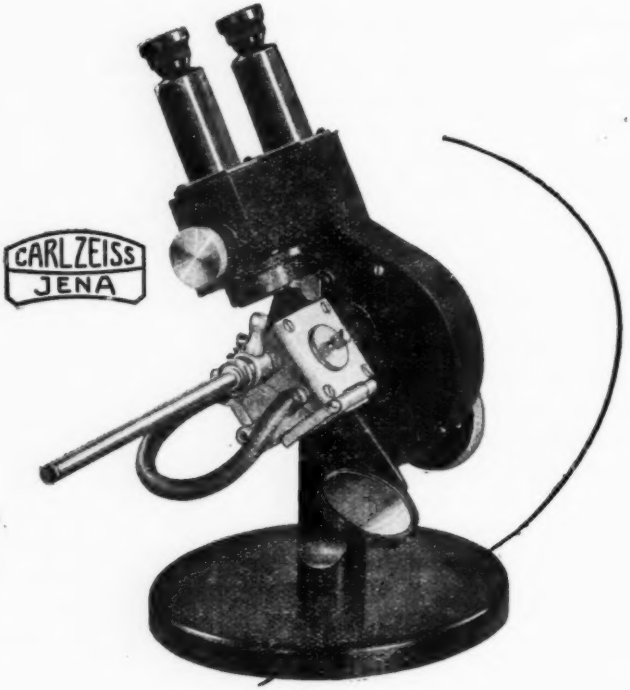

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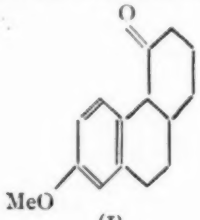
[Jour. Indian Chem. Soc., Vol. 36, No. 4, 1959]

SYNTHESIS OF 4-KETO-7-METHOXY-1 : 2 : 3 : 4 : 4a : 9 : 10 : 10a-OCTAHYDRO-PHENANTHRENE

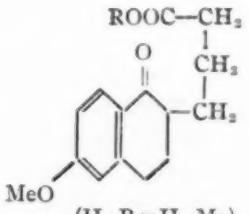
By D. K. Banerjee[1] and S. K. Das Gupta[2]

4-Keto-7-methoxy-1 : 2 : 3 : 4 : 4a : 9 : 10 : 10a-octahydrophenanthrene has been prepared as a model for the synthesis of aromatic analogues of 11-keto-steroids.

In this communication model experiments leading to the synthesis of 4-keto-7-methoxy-1 : 2 : 3 : 4 : 4a : 9 : 10 : 10a-octahydrophenanthrene (I), prior to their application for the preparation of aromatic analogues of 11-keto-steroids, have been described. The key intermediate, γ-2-(1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthyl)-butyric acid (II : R = H), was prepared as described below.

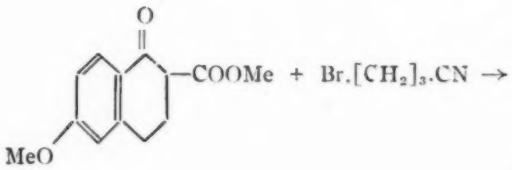


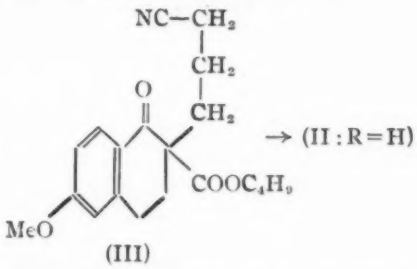
(I)



(II : R = H, Me)

Methyl 6-methoxytetralone-2-carboxylate, prepared by the method of Bachmann and Thomas (*J. Amer. Chem. Soc.*, 1942, **64**, 94), was condensed with γ-bromobutyronitrile in the presence of potassium butoxide[1]. The resulting cyano-ester (III) was hydrolysed and decarboxylated by refluxing with dilute hydrochloric acid. Bachmann and Wendler (*ibid.*, 1946, **68**, 2580) had observed the formation of some phenol under such condition of hydrolysis of compounds containing phenolic ether group. In order to avoid the loss due to demethylation, the crude hydrolysed product was treated with dimethyl sulphate in aqueous sodium hydroxide, and the crystalline γ-2-(1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthyl)-butyric acid was obtained in good yield.





(III)

Other attempts to prepare the keto-acid (II : R = H) have also been recorded. Initial steps of one of these consisted in the condensation of diethyl (2-*m*-methoxyphenylethyl)-malonate (Bachmann, Kushner and Stevenson, *ibid.*, 1942, **64**, 974) with

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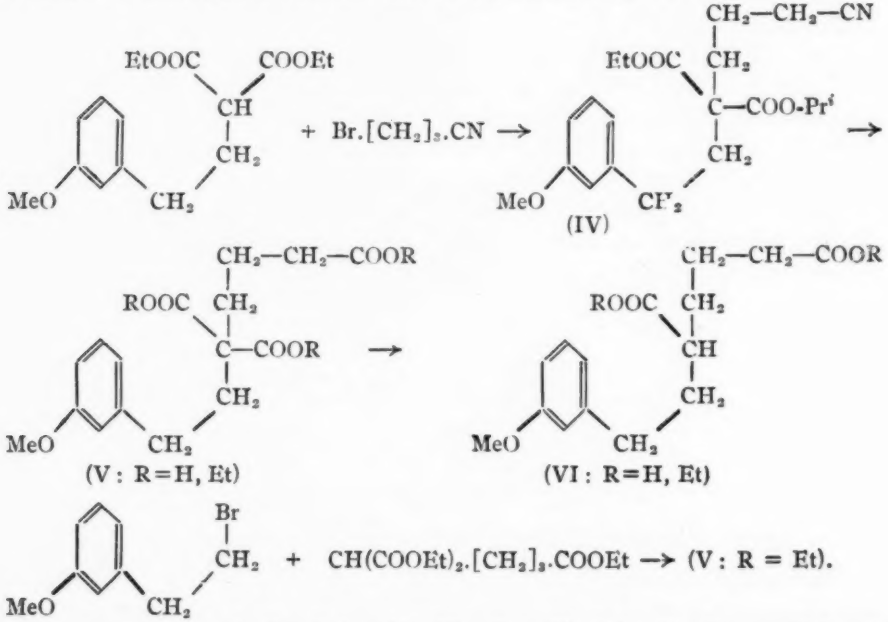
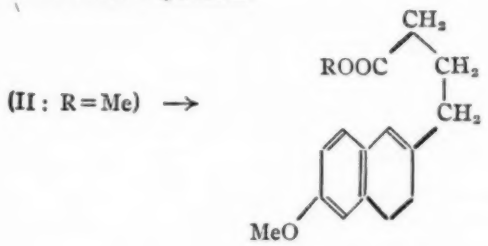
γ-bromobutyronitrile in the presence of potassium propoxide[4], followed by saponification of the condensation product (IV), which was obtained in 80% yield. The crude malonic acid derivative (V : R=H), thus obtained, was heated for an hour at 180°, and then esterified. The analytical values for the product agreed well with those of diethyl (2-*m*-methoxyphenylethyl)-(3-ethoxycarbonylpropyl)-malonate (V : R= Et) ; presumably the malonic acid derivative (V : R=H) was resistant to decarboxylation. In another experiment, 2-*m*-methoxyphenylethyl bromide was condensed with diethyl (3-ethoxycarbonylpropyl)-malonate (Donin *et al.*, *ibid.*, 1951, **73**, 4256) in the presence of potassium butoxide[4] to furnish the aforementioned tri-ester (V : R=Et), which after a preliminary treatment with refluxing concentrated hydrochloric acid was heated with 20% aqueous potassium hydroxide. The malonic acid derivative (V : R=H) was obtained as a crystalline solid under these conditions along with some gummy acidic material. The latter on esterification yielded diethyl α-(2-*m*-methoxyphenylethyl)-adipate (VI : R=Et). This ester was obtained in an improved yield when the tri-ester (V : R=Et) was subjected to a prolonged treatment with refluxing hydrochloric acid, followed by esterification.

α-(2-*m*-Methoxyphenyl)-adipic acid (VI : R = H), obtained by saponification of (VI : R=Et), was converted into the acid chloride, and the latter was treated *in situ* with stannic chloride. The resulting product could not be induced to crystallise, but the analytical values agreed well with those of the keto-acid (II : R=H).

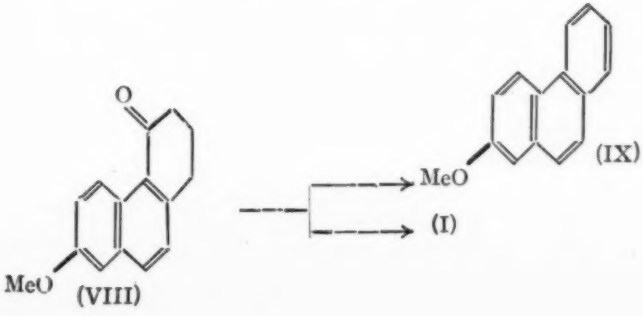


For conversion of the keto-acid (II : R = H) into (I), the methyl ester of the former was treated with a boiling solution of aluminium propoxide[4] in dry toluene containing a very small quantity of propyl[4] alcohol, and the resulting crude product was dehydrated by heating with fused potassium hydro-

gen sulphate to yield the unsaturated ester (VII: R = (Pr^i). The ultraviolet absorption spectrum of (VII: R = Pr^i) exhibited a maximum at 272.5 mμ (log ϵ 4.1), indicating the presence of *p*-methoxystyrene group (Woodward, *ibid.*, 1944, **66**, 676). Saponification of the unsaturated ester furnished the crystalline γ-2-(6-methoxy-3:4-dihydronaphthyl)-butyric acid (VII: R=H). The ring-closure experiment with (VII: R=H) was carried out with acetic anhydride and fused zinc chloride at ther oom temperature and also at the refluxing temperature of the reaction mixture to obtain the unsaturated ketone in 53% and 40% yields respectively. This is in agreement with the observation of Bachmann and Dreiding (*J. Org. Chem.*, 1948, **13**, 317) that the six-membered ring ketones are formed in better yields at lower temperatures under these conditions. The ultraviolet absorption spectrum of (VIII) is of interest in exhibiting a maximum at 245.5 mμ (log ϵ 4.3), characteristic of an $\alpha:\beta:\beta$-substituted unsaturated ketone (Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 76), and another at 310 mμ (log ϵ 3.7), the absorption maximum at 272 mμ due to *p*-methoxystyrene group being absent. The unsaturated ketone (VIII) was catalytically hydrogenated to the saturated ketone (I), which after a treatment with potassium butoxide^t was recovered unchanged, as evidenced by the formation of a semicarbazone, identical with that of the untreated ketone. This fact suggests that the two hydroaromatic rings in (I) are mainly in the stable *trans* relationship to one another. In order to confirm the nuclear structure of (VIII), the product was treated with $LiAlH_4$ and the resulting crude carbinol was dehydrated with potassium hydrogen sulphate, followed by dehydrogenation with palladium-charcoal, when the known 2-methoxyphenanthrene (IX) was obtained in good yield. The melting point of the picrate of (IX) was not depressed on admixture with an authentic specimen.



[VII: R=H, Pr^i]



EXPERIMENTAL*

γ-2-(1-Keto-2-butoxy^t carbonyl-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthyl)-butyronitrile (III).—To a solution of potassium butoxide^t, prepared from potassium (2.3 g., 0.059 *M*) in butanol^t (55 c.c.), methyl 6-methoxytetralone-2-carboxylate (12.84 g., 0.55 *M*) in dry benzene (55 c.c.) was added in the cold, resulting in a light orange-coloured solution. γ-Bromobutyronitrile (8.8 g., 0.059 *M*) in dry benzene (10 c.c.) was then added to it, and the mixture, on keeping for 16 hours, was refluxed for 12 hours. After removal of the solvent under diminished pressure, water was added and the product extracted with ether. The extract was washed with cold 2% aqueous NaOH and water, and the solvent was removed. The residue was subjected to short path distillation, and the fraction, b.p. 160-70°/0.05 mm, was collected, yield 9.4 g. (50%). (Found: C, 69.99 ; H, 7.2. $C_{20}H_{25}O_4N$ requires C, 69.97 ; H, 7.29%). The analytical values indicate a butyl^t ester exchange during the above condensation.

γ-2-(1-Keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthyl)-butyric Acid (II : R=H).—A mixture of the keto-cyano ester (III, 8.34 g), HCl (100 c.c.) and water (100 c.c.) was refluxed for 12 hours. The volatile products were removed completely under diminished pressure. The residue was dissolved in 10% aqueous NaOH (40 c.c.) and treated with dimethyl sulphate (6 c.c.) at 50-60°. NaOH (4.1 g.) was next added to the reaction mixture, which was then heated for 2 hours on a steam-bath. After cooling and dilution with water, the neutral material was removed by extraction with ether, and the alkaline solution was acidified and extracted with benzene (3 × 50 c.c.). The extract was washed with water, the solvent removed, and the residue purified by short path distillation, b.p. 155°/0.05 mm. The product crystallised on cooling, crude m.p. 95°, yield 5.4 g. (84%). After recrystallisation from ether-pet. ether (40-60°) the keto-acid (II : R=H) melted at 99°. (Found: C, 68.60 ; H. 6.42. $C_{15}H_{18}O_4$ requires C, 68.70 ; H, 6.87%).

Methyl γ-2-(1-Keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthyl)-butyrate (II : R=Me).—A solution of the acid (II : R=H) in benzene was treated with an ethereal solution of diazomethane, prepared from nitrosomethylurea (3.3 g.). After allowing it to stand for 15 minutes, the methyl ester was worked up in the usual manner. The product was purified by short path distillation, b.p. 125°/0.05 mm, and crystallised from ether-pet.-ether (40-60°), m.p. 74°, yield 5 g. (94%), λ_{max} 226 mμ (log ε 4.0), λ_{max} 276 mμ (log ε 4.1), λ_{min} 240 mμ (log ε 3). (Found: C, 69.92 ; H, 7.67. $C_{16}H_{20}O_4$ requires C, 69.56 ; H, 7.25%).

iso*Propyl γ-2-(6-Methoxy-3 : 4-dihydronaphthyl)-butyrate* [VII : R = Pr^i].—A solution of methyl γ-2-(1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthyl)-butyrate (4.8 g., 0.017 *M*), aluminium propoxide^t (12 g., 0.06 *M*), dry toluene (40 c.c.) and anhydrous propanol^t (1 c.c.) was refluxed for 4 hours. Propanol^t (40 c.c.) was added to it and distilled out in 1 hour through a fractionating column. The latter operation was repeated twice. The reaction mixture was decomposed with cold 10% H_2SO_4. The toluene layer was separated and the aqueous layer extracted with ether (2 × 50 c.c.). The residue (4 g.), obtained after removal of the solvent mixture, was

* All melting points are uncorrected. The ultraviolet absorption spectrum was determined in ethanol (95%) by the Unicam spectrophotometer, S. P. 500.

heated with $KHSO_4$ (10.5 g.) for 1 hour at 160°. The ether extract of the cooled material was washed with water, and the solvent removed. The residual oil was subjected to short path distillation, and the fraction, b.p. 125°/0.05 mm, collected; yield 2.4 g. (50%), λ_{max} 272.5 mμ (log ε 4.1). (Found: C, 75.51; H, 8.58. $C_{18}H_{24}O_3$ requires C, 75.00; H, 8.33%). Analytical values indicate a propyl[i] ester exchange during the reaction.

γ-2-(6-*Methoxy*-3:4-*dihydronaphthyl*)-*butyric Acid* (VII: R=H).—A mixture of the unsaturated ester (VII: R = Pr[i]) (2.4 g.), 10% aqueous KOH (20 c.c.) and 95% ethanol (20 c.c.) was refluxed for 3 hours. The volume of the reaction mixture was reduced to half by evaporation before dilution with water. After removal of the neutral material by extraction with ether, the aqueous solution was acidified and extracted with ether. The solvent was removed and the residue purified by short path distillation, b. p. 135°/0.05 mm. The product, on cooling, crystallised, m. p. 80°, yield 2 g. (96%). (Found: C, 73.42; H, 7.48. $C_{15}H_{18}O_3$ requires C, 73.17; H, 7.32%).

4-*Keto*-7-*methoxy*-1:2:3:4:9:10-*hexahydrophenanthrene* (VIII).—(*a*). A solution of the acid (VII: R=H; 1 g.), acetic anhydride (100 c.c.) and a freshly prepared 20 mg./c.c. solution of fused zinc chloride in acetic anhydride was refluxed for 4 hours in an atmosphere of nitrogen. The acetic anhydride was decomposed by dropwise addition of water (100 c.c.) to the still hot dark brown solution, and the acetic acid removed on a steam-bath in a current of nitrogen. The residue was taken up in ether, washed with dilute aqueous ammonia and water, and then dried over anhydrous sodium sulphate. The solvent was removed and the residue subjected to short path distillation, when a thick oil, b.p. 125°/0.05 mm, was obtained; yield 0.4 g. (41%), λ_{max} 245.5 mμ (log ε 4.3), λ_{max} 310 mμ (log ε 3.7). (Found: C, 78.49; H, 7.73. $C_{15}H_{16}O_2$ requires C, 78.95; H, 7.02%).

(*b*). A solution of the unsaturated acid (VII: R=H; 1 g.) in acetic anhydride (13.7 c.c.) and a 5% solution of fused zinc chloride in glacial acetic acid (2.8 c.c.) were allowed to stand for 20 hours at the room temperature under nitrogen. The solution assumed different shades of colour and finally turned red. It was then heated for 1 hour at 70°. The reaction mixture, after cooling, was taken up in ether and thoroughly washed with chilled 5% aqueous NaOH and finally with water. The neutral residue, after removal of the solvent, was purified by distillation to yield the unsaturated ketone (VIII) (0.5 g., 53%).

The *semicarbazone* was obtained in the usual manner in 75% yield, crude m.p. 110°; crystallised from 95% ethanol, m.p. 116° (vac.). It turned yellow on keeping. (Found: C, 67.98; H, 7.11. $C_{16}H_{19}O_2N_3$ requires C, 67.38; H, 6.67%).

4-*Keto*-7-*methoxy*-1:2:3:4:4a:9:10:10a-*octahydrophenanthrene* (I).—The unsaturated ketone (VIII, 1 g.) in ethanol was stirred in an atmosphere of hydrogen with 5% Pd—C (0.4 g.) until the absorption of hydrogen was complete. Ether was added and the solution filtered from the catalyst, and the solvent was removed. Short path distillation of the residue, b.p. 120°/0.05 mm, afforded the reduced ketone (I) as a liquid; yield 0.91 g. (91%), λ_{max} 273 mμ (log ε 3.2). (Found: C, 78.11; H, 7.64. $C_{15}H_{18}O_2$ requires C, 78.27; H, 7.83%).

The *semicarbazone*, prepared by the usual method, was crystallised from 95% ethanol, m.p. 136°. (Found : C, 67.21 ; H, 7.41. $C_{16}H_{21}O_2N_3$ requires C, 66.9 ; H, 7.32%).

Treatment of (I) *with Potassium Butoxide*[4].—The ketone (I, 0.15 g.) in butanol[4] (5 c.c.) was added to a solution of potassium butoxide[4], prepared from potassium (1 g.) in butanol[4] (20 c.c.). On keeping in an atmosphere of nitrogen at the room temperature for 2½ hours, the mixture was treated with an excess of ammonium chloride and the butanol[4] removed under diminished pressure. It was extracted with ether, and the ethereal solution was washed with water and dried, and the solvent removed. Short path distillation of the residue afforded a liquid, which was directly converted to its semicarbazone. The latter after crystallisation from 95% ethanol melted at 136°. The mixed melting point with the semicarbazone of (I) was not depressed.

Conversion of 4-Keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene to 2-Methoxyphenanthrene (IX).—A slurry of $LiAlH_4$ (0.15 g.) in dry ether (30 c.c.) was added to a solution of the unsaturated ketone (VIII, 0.8 g.) in dry ether (15 c.c.). After refluxing for 2 hours, the cooled solution was decomposed by careful addition of 10% H_2SO_4. The ether layer was separated and washed with water, saturated bicarbonate solution and water successively, and dried over anhydrous sodium sulphate. The residual oil, after removal of the solvent, was dried under vacuum and heated with freshly fused $KHSO_4$ (1.5 g.) for 15 minutes at 200° in an atmosphere of nitrogen. Short path dtstillation of the mixture furnished an oily material which was directly dehydrogenated by heating with 30% Pd—C (0.6 g.) for 30 minutes at 225-28° in a Heymann type of apparatus. The product was dissolved in benzene-ether mixture and filtered. The dry residue, obtained after removal of the solvent, was purified by distillation, when 2-methoxyphenanthrene (IX) was obtained as colorless crystalline plates, m.p. 95-96° ; yield 0.51 g. (70%) ; it was crystallised from 95% ethanol, m. p. 99°. (Found : C, 86.74 ; H, 6.02. $C_{15}H_{12}O$ requires C, 86.54 ; H, 5.77%).

The *picrate*, prepared in the usual manner, melted in the crude state at 120° ; on recrystallisation from 95% ethanol, it melted at 124°, which remained undepressed on admixture with an authentic specimen.

1-m-Methoxyphenyl-3-ethoxyphenyl-3-propoxy[4]carbonyl - 6-cyanohexane (IV).—Ethyl (2-*m*-methoxyphenylethyl)-malonate (19.28 g., 0.06 *M*) in dry benzene was added to a solution of potassium propoxide[4], prepared from potassium (2.7 g., 0.07 *M*), dry benzene (75 c.c.), and propanol[4] (50 c.c.). To it with cooling in ice was added γ-bromobutyronitrile (13.37 g., 0.09 *M*) in dry benzene (20 c.c.). The mixture was allowed to stand for 17 hours and then refluxed for 16 hours, when the reaction mixture was very faintly alkaline to litmus. It was cooled, diluted with a large volume of water and extracted with ether. The extract was washed with brine solution and dried over calcium chloride. The residue, after removal of the solvent, was distilled, and the fraction, b.p. 210-15°/1 mm, was collected ; yield 19 g. (80%). (Found : C, 67.34 ; H, 7.71. $C_{21}H_{29}O_5N$ requires C, 67.20 ; H, 7.73%). Analytical values indicate an propyl[4] ester exchange during the condensation.

1-m-*Methoxyphenyl*-3 : 3 : 6-*triethoxycarbonylhexane* (V : R = Et).—(*a*). The aforementioned cyanomalonic ester (IV, 18.5 g.) was refluxed for 23 hours with a solution of KOH (22 g.) in water (80 c.c.). The solution was acidified in the cold, extracted with ether (3 × 100 c.c.), and the ether removed. The residue, after being dried by heating on a steam-bath under vacuum, was placed in a preheated oil-bath at 180-85° for half an hour. The cooled product was then refluxed for 18 hours with a mixture of dry ethanol (80 c.c.) and H_2SO_4 (conc., 15 c.c.). The ester was worked up in the usual manner and distilled under vacuum. The major fraction, b.p. 215-20°/1.5 mm, was obtained as a viscous liquid, yield 11 g. (Found : C, 65.02 ; H, 7.65. $C_{22}H_{32}O_7$ requires C, 64.71 ; H, 7.84%). The high boiling point and the analytical values indicate that the crude malonic acid derivative is hardly decarboxylated under the conditions of the aforementioned experiment.

(*b*). *Condensation of* 2-m-*Methoxyphenylethyl Bromide with Diethyl* (3-*Ethoxycarbonylpropyl*)-*malonate*.—To an ice-cold solution of potassium butoxide[t], prepared from potassium (3.9 g., 0.1 *M*) and dry butanol[t] (94 c.c.), were added first diethyl (3-ethoxycarbonylpropyl)-malonate (27.4 g., 0.1 *M*) and then, with further cooling in ice and salt, a solution of 2-*m* methoxyphenylethyl bromide (21.5 g., 0.1 *M*) in dry benzene (20 c.c.). After keeping for 16 hours, the reaction mixture was refluxed for 10 hours. The solvent was removed under diminished pressure, and the cooled residue after dilution with water was extracted with benzene (3 × 100 c.c.). The extract was washed successively with water, sodium bicarbonate solution and water. The residue after removal of the solvent was distilled, and the fraction, b.p. 210-15°/1 mm, was collected; yield 8.63 g. (21%). (Found : C, 65.12 ; H, 7.87. $C_{32}H_{32}O_7$ requires C, 64.71 ; H, 7.84%).

Hydrolysis of Diethyl (2-m-*Methoxyphenylethyl*)-(3-*ethoxycarbonylpropyl*)-*malonate*

(*a*). (2-m-*Methoxyphenylethyl*)-(3-*oxycarbonylpropyl*)-*malonic Acid* (V : R = H).—The triester (V : R = Et, 4.3 g.) was refluxed for 4 hours with 10% HCl (100 c.c.). It was cooled, extracted with ether, and the ether removed. The dried residue was refluxed for 4 hours with a solution of KOH (3.9 g.) in water (27 c.c.). The cooled solution after extraction with ether to remove any neutral material, was acidified in the cold. The acidic material was extracted with ether (2 × 50 c.c.). On removal of the solvent a gummy residue (2.8 g.) was obtained, which on trituration with 1 : 2 ether-benzene (10 c.c.) afforded a crystalline material (0.9 g.), m.p. 147° (decomp.). After two crystallisations from ether-benzene, the product melted at 155° (decomp.). (Found : C, 59.74 ; H, 6.27. $C_{16}H_{20}O_7$ requires C, 59.27 ; H, 6.17%).

Diethyl α-(2-m-*Methoxyphenylethyl*)-*adipate* (VI : R = Et).—The residual non-crystalline portion of the aforementioned acidic material was esterified by refluxing with ethanol (20 c.c.) and H_2SO_4 (conc. 1.5 c.c.). On working up in the usual manner, a fraction, b.p. 190-95°/1.5 mm, was obtained. (Found : C, 67.35 ; H, 8.35. $C_{19}H_{28}O_5$ requires C, 67.86 ; H, 8.33%).

(*b*). α-(2-m-*Methoxyphenyl*)-*adipic Acid* (VI : R = H).—The tri-ester (V : R = Et ; 11 g.) was refluxed for 19 hours with HCl (*d* 1.15, 95 c.c.). The cooled solution was

extracted with ether-benzene mixture. The solvent was removed and the crude residue was refluxed for 18 hours with ethanol (80 c.c.) and H_2SO_4 (conc., 15 c.c.). The ester was worked up as usual and distilled to give a fraction, b.p. 190-95°/1.5 mm, yield 7.5 g. (83%). (Found : C, 67.27 ; H, 8.35. $C_{19}H_{28}O_5$ requires C, 67.86 ; H, 8.33%).

The aforementioned ester (7.5 g.) was refluxed for 15 hours with a solution of KOH (9 g.) in water (33 c.c.). The acidic material was worked up as usual and on short path distillation yielded a thick glass, b.p. 200°/0.05 mm, yield 5 g. (Found : C, 64.91 ; H, 7.23. $C_{15}H_{20}O_5$ requires C, 64.27 ; H, 7.13%).

Ring-closure Experiment with α-(2-m-*Methoxyphenylethyl*)-*adipic Acid*.—Finely powdered PCl_5 (11.6 g., 0.056 *M*) was added to a stirred and cold solution of the di-acid (VI : R=H ; 5 g., 0.014 *M*) in dry benzene (32 c.c.), and the mixture was allowed to stand for 2 hours. After further cooling in an ice-bath, the stirred mixture was treated with a chilled solution of stannic chloride (4.9 c.c., 0.042 *M*) in dry benzene (16 c.c.). The mixture was stirred for another 15 minutes and the product was poured into a mixture of crushed ice, HCl (conc., 50 c.c.), and ether 50 c.c. The mixture was gently swirled until the two layers clearly separated out. The organic layer was washed with cold 10% HCl (3 × 50 c.c.) and water, dried, and the solvent removed. The residue on short path distillation yielded a glassy material, b.p. 180°/0.05 mm, yield 2.3 g. (50%). The product could not be induced to crystallise but its analytical values agreed with those for the keto-acid (II : R=H). (Found : C, 68.20 ; H, 6.17. $C_{15}H_{18}O_4$ requires C, 68.70 ; H, 6.87%).

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APPLICATION OF GLYCOLIC TITRATION. PART IV. TITRATION OF ACIDS AND ACID MIXTURES

By Ch. Kalidas and Mihir Nath Das*

Glycolic solvent mixtures have been successfully used for titration of various weak bases which are too weak to be titrated in water. The titration can very conveniently be done with the help of a *p*H meter, and for the relatively strong bases, the titration can also be followed with the help of suitable indicators. It has been observed that glycolic solvents, in general, enhance the strengths of weak bases and, hence, accentuate the end-point. Thus, glycol essentially behaves as an 'acidic' solvent. This property presumably arises from the high hydrogen-bonding power of this solvent as a consequence of the contiguity of two hydroxyl groups.

It is well known that basic solvents exert a "levelling effect" on acids, whereas acidic solvents, in general, tend to have a differentiating effect on various acids. The differentiating effect of glacial acetic acid on the strengths of various mineral acids, which all appear to be almost equally strong in water, is a typical, though rather extreme, example of this phenomenon (Kolthoff and Willman, *J. Amer. Chem. Soc.*, 1934, **56**, 1007). Glycol, being an acidic solvent in a wider sense of the term, may reasonably be expected to exert a similar, though weaker, differentiating effect on the strengths of acids and should therefore serve as a medium for differential titration acid mixtures, in cases where such titration is not successful in aqueous medium.

Palit (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 246) reported that by using ethylene-glycol-*iso*propanol (1 : 1) as a titration medium, it was possible to obtain two inflections by titrating sulphuric acid with sodium hydroxide in the same solvent. It may be noted here that the same titration in water affords only one inflection, corresponding to the complete neutralisation of the acid. Palit further reported that by using the same solvent medium, three inflections were obtained for a mixture of sulphuric and acetic acids. A mixture of nitric and sulphuric acids also gives two inflections, when titrated in the same solvent mixture. Das and Mukherjee (unpublished work) have successfully used glycolic solvent media for differential titration of several acid mixtures, binary and ternary, containing sulphuric acid as a common constituent. The object of the present work has been to explore further possibilities regarding the application of glycolic solvents for differential titration of various acid mixtures and of polybasic acids. Many other solvents have been used for differential titration of different acid mixtures. Glacial acetic acid (Shkodin and Izmailov, *J. Gen. Chem.*, U.S.S.R., 1950, **20**, 39), ketonic solvents (Izmailov *et al.*, *ibid.*, 1939, **9**, 453, 598 ; Shkodin, *ibid.*, 1940, **10**, 1694), acetonitrile (Kilpatrick, *Chem. Rev.*, 1933, **13**, 131 ; Lavine and Toennis, *J. Biol. Chem.*, 1933, **101**, 727 ; Critchfield and Johnson, *Anal. Chem.*, 1954, **26**, 1803), alcohols (Evans and Davenport, *J. Amer. Chem. Soc.*, 1937, **59**, 1920 ; *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 287), dimethylformamide and ethylene-diamine (Moss, Elliot and Hall, *Anal. Chem.*, 1948, **20**, 784 ; Deal and Wyld, *ibid.*,

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1955, **27**, 47) have been used by different workers for this purpose. Glycolic solvents admittedly possess distinct advantages over many other organic solvents as a titration medium (Palit, Das and Somayajulu, An. Rep. Indian Assoc. Cult. Sci., 1959) and hence it has been deemed worthwhile to undertake the present investigation.

EXPERIMENTAL

A mixture of ethyleneglycol (B.D.H – L.R) and *iso*propanol (1 : 1) was employed throughout the investigations. The ethyleneglycol sample was tested for basic impurities and a blank correction was applied when necessary. *iso*Propanol was purified by the following procedure. The original sample was found to contain some pyridine (added as a denaturant) and a good amount of water. To a litre of the impure sample, about 20 g. of oxalic acid was added. The mixture was refluxed for 2 to 3 hours and then distilled. The distillate was treated with freshly burnt quicklime, kept overnight and redistilled, the middle fraction at 82-83° being collected.

Preparation and Standardisation of Acid Solutions.—A known amount of the acid was dissolved in the requisite volume of the mixed solvent to give a solution of the desired strength, usually decinormal.

The solutions of the strong acids were standardised as follows. A weighed amount of sodium carbonate (A.R.) was taken and converted into acetate by gentle heating with a few drops of glacial acetic acid. The solution was cautiously evaporated to dryness. The residue was taken up with the mixed solvent and titrated with the acid to be standardised, using thymol blue as indicator. A little chloroform was added towards the end of the titration to sharpen the end-point, which was registered by a sharp colour change from yellow to light pink.

The solutions of weak acids were standardised against a standard alkali solution by potentiometric titration.

Solution of Bases.—A solution of NaOH in glycolic solvents can be used as the standard base. But, for most of the present work, the alkali solution used was prepared by dissolving metallic sodium directly in ethyleneglycol.

The resulting solution may contain sodium glycolate, but most probably the moisture present in glycol converts it into sodium hydroxide. Any way, this is immaterial for titration purposes. A freshly cut piece of metallic sodium (roughly weighed) was placed in a desired quantity of glycol, and after the reaction had subsided, the solution was diluted with an equal volume of *iso*propanol. The alkali solution so obtained was standardised against standard perchloric or hydrochloric acid in the same solvent, using thymol blue as indicator.

There are certain disadvantages in using an alkali solution as a standard base for titration of acids, especially for acid mixtures. It tends to absorb carbon dioxide from air, forming carbonate. Moreover, an alcoholic solution of alkali, in general, has a tendency to undergo aerial oxidation leading to the formation of salts of organic acids. These salts behave as bases in glycolic solvents and introduce uncertain factors in the titration results. Aged solutions of alkali therefore are not suitable for titration of acids. The solutions of alkali must be freshly prepared and preserved in well-stoppered bottles.

Triethylamine as a decinormal solution in the mixed solvent, and standardised as above, was also used for titration of some acids.

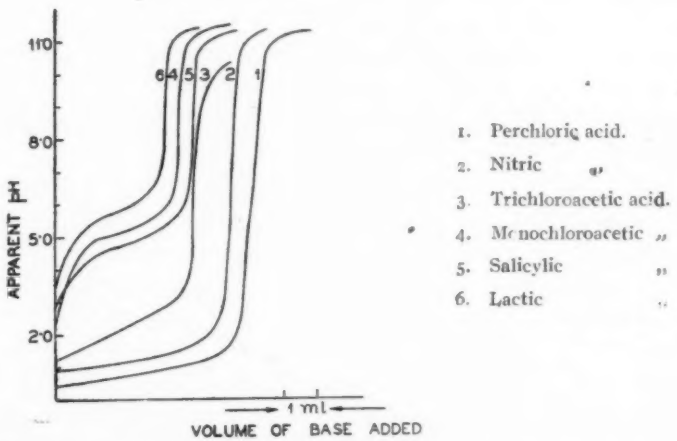
Sodium acetate was also used for titration of acids, and a standard solution of this base was prepared by dissolving weighed amount of A.R. sodium carbonate in a small amount of glacial acetic acid and then cautiously evaporating and dissolving it in the solvent mixture which should be exactly neutralised before preparing the solution. Otherwise, the solution should be standardised against a standard acid.

Procedure.—The general experimental procedure for potentiometric titration was essentially the same as recommended by Palit *et al.* (*loc. cit.*) for titration of bases. A Cambridge *p*H meter was used for the work to record the values of apparent *p*H of the solution during titration, stirring being effected by an electromagnetic device.

Discussion

Titration of Monobasic Acids.—Fig. 1 shows the curves for titration of several monobasic acids against alkali solution. Titration was also carried out against the bases, triethylamine and sodium acetate (the curves are not represented here). It will be seen that perchloric and nitric acids are equally strong in this medium. Trichloroacetic acid behaves as a fairly strong acid in glyclolic solvents, though weaker than the mineral acids. These strong acids can be titrated with any of the three bases mentioned above. The inflection is naturally the most pronounced with the alkali being followed by that obtained with triethylamine. Sodium acetate is a much weaker base than the amine, as judged by the sharpness of the inflection point. Triethylamine cannot be used for titration of acids weaker than those with values of K_a of the order of 10^{-3} in water. For weaker acids, the inflection is not sharp.

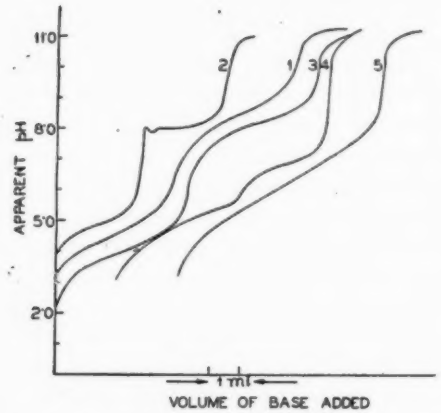
Fig. 1



Titration of Polybasic Acids.—Fig. 2 represents the titration curves obtained for a number of polybasic acids against alkali.

It is interesting to note that phthalic acid gives two well-defined inflections corresponding to its dibasic nature in glycolic solvents. In *iso*propanol alone, phthalic acid gives two inflections, but here, there is a disadvantage in that the sodium salt formed precipitates out copiously just before or after the first inflection point, thus affecting the titration curves. Addition of glycol, though reducing the inflection, exercises a greater solvent effect, and no precipitation usually occurs during the course of titration. For phthalic acid, glycolic titration is decidedly superior to titration in water, since this acid gives only a feeble inflection corresponding to its first hydrogen in aqueous medium, which cannot be utilised for analytical purposes. Moreover, the solubility of phthalic acid is higher in glycolic solvents than in water.

FIG. 2



1. Phthalic acid.
2. Do in *iso*propanol.
3. Phosphoric acid
4. Tartaric acid.
5. Citric acid.

Phosphoric acid also gives two well-defined inflections corresponding to the first two hydrogen atoms. The third hydrogen cannot be titrated in glycolic solvents. A feature of the glycolic titration is that the solvent reduces the acid strength of phosphoric acid, glycol being an acidic solvent. Hence, the inflections are somewhat sharper in water than those in glycolic solvents. It can also be seen that phthalic and phosphoric acids are of nearly equal strength in glycolic solvents.

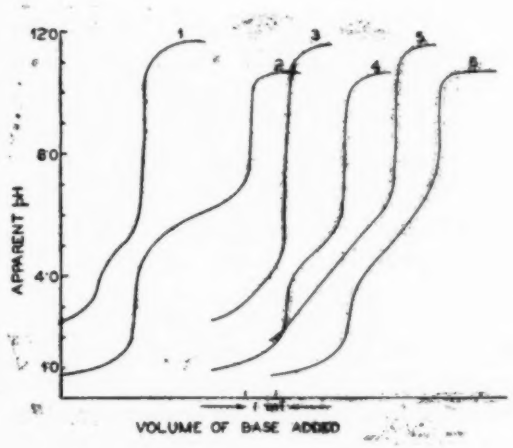
Tartaric acid tends to give a feeble first inflection, whereas citric acid yields only one inflection corresponding to total neutralisation. The titration of oxalic acid is rather interesting. From a study of its dissociation constants, it is reasonable to expect two inflections, when oxalic acid in ethyleneglycol-*iso*propanol (1 : 1) is titrated against alkali in the same solvent. But the precipitation of sodium mono-oxalate at or near the first inflection point results in a slight lowering of *p*H, thereby masking the first inflection. Thereafter, the titration can be continued without any further difficulty.

In the case of sulphuric acid also, Das and Mukherjee (*loc. cit.*) have observed that a similar precipitation of sodium sulphate occurs at a certain stage after the first inflection and has a similar effect on the *p*H, which shows a decrease and then attains a constant value after equilibrium has been attained.

The titration of sulphurous acid is one of much practical difficulty because sulphur dioxide is sparingly soluble in glycolic solvents. Consequently, while titration is being carried out, some of the sulphur dioxide gas escapes while a part of it tends to undergo aerial oxidation.

Titration of Mixtures of Acids.—Using the information obtained regarding the relative strengths of acids from the titration curves, a few differential titrations of acid mixtures were carried out. Thus, picric acid can be differentially titrated in the presence of acetic formic or citric acid. The corresponding curves for water as titration medium have been drawn alongside for comparison. It is obvious that glycolic solvents are superior to water as titration media for such acid mixtures. Fig. 3 shows the curves obtained for a mixture of picric acid with acetic, formic and citric acid respectively.

FIG. 3

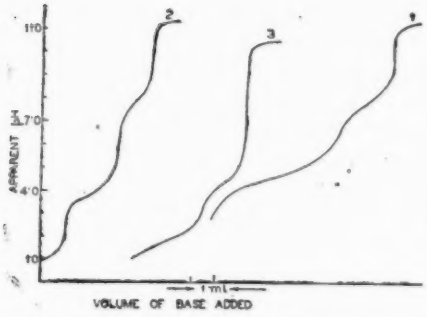


1. Picric & acetic acids in water.
2. Do in ethyleneglycol : *iso*propanol (1 :1).
3. Picric & formic acids in water.
4. Do in ethyleneglycol : *iso*propanol (1 :1).
5. Picric & citric acids in water.
6. Do in ethyleneglycol : *iso*propanol (1 :1).

By virtue of the two inflections obtained for phthalic acid in glycolic media, it is possible to titrate a mixture of phthalic and salicylic acids. Salicylic acid is titrated along with the first hydrogen of phthalic acid, so that the first inflection corresponds to half phthalic acid + salicylic acid, while the second inflection corresponds to the total neutralisation. The amount of salicylic acid present should not exceed that of phthalic acid.

Similarly, a mixture of phthalic and sulphuric acids gives three inflections in glycolic solvent. The first inflection corresponds to the first hydrogen of sulphuric acid + the first hydrogen of phthalic acid, while the third one corresponds to the second hydrogen of phthalic acid. Thus, a mixture of phthalic and sulphuric acids can be analysed.

FIG. 4



1. Phthalic & salicylic acids in E. G.- *iso*propanol (1:1).
2. Do H_2SO_4 ,, ,,
3. Tri- & mono-chloroacetic acids ,, ,,

Similarly a mixture of trichloroacetic and monochloroacetic acids was found to give two inflections when titrated against alkali in glycolic media. The amount of trichloroacetic acid present should be at least three times that of monochloroacetic acid. Otherwise, the first inflection is very poor. Fig. 4 shows all the curves obtained for the titration of these acid mixtures.

The following table summarises the results of the differential titrations carried out.

TABLE I

No.	Mixture of acids titrated.	No. of inflections.	Remarks.
1.	Picric + acetic	2	Both are strong.
2.	Picric + formic	2	Second inflection very strong while the first one slightly weaker.
3.	Picric + citric	2	First inflection decidedly weaker than the second.
4.	Phthalic + salicylic	2	Both are of the same magnitude.
5.	Phthalic + sulphuric	3	All the three are quite strong.
6.	Trichloro- + monochloro-acetic	2	First inflection very weak.

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REACTION BETWEEN PERSULPHATE AND OXALATE IN PRESENCE OF MANGANESE (II)

By Yugul Kishore Gupta and Satyeshwar Ghosh

Mn^{II} is ordinarily not oxidised by persulphate, but in presence of oxalate, red-coloured oxalate complex of Mn^{III} is obtained. This may also be regarded as oxidation of oxalate by persulphate in presence of Mn^{II}. The reaction mixture gradually turns red and finally becomes colorless, but there is no loss of oxidant estimated iodometrically, or of the reductant, estimated by the permanganate. A mechanism has been proposed for the appearance and the disappearance of the red-coloured complex. It has been suggested that the free radical OH, which ordinarily oxidises oxalate, is co-ordinated to another free radical SO_4^- to form Caro's acid which liberates iodine like persulphate from KI. Thus, no oxalate is oxidised and no decrease in the oxidant takes place.

Oxidation of oxalate by persulphate is very slow at ordinary temperatures. It was thought that Mn^{II} may act as a catalyst in this reaction as it does in the oxidations by permanganate and dichromate (Gupta and Ghosh, *Z. physikal. Chem.*, 1958, **208**, 368 ; Chakravarti and Ghosh, this *Journal*, 1957, **34**, 841). It was found that in presence of Mn^{II}, red-coloured trivalent manganese was formed which reached a maximum concentration and finally passed off. The trivalent manganese could be estimated colorimetrically, but this only gave the difference of the amount of trivalent manganese formed and the amount reduced by the oxalate at any instant. In order to calculate the actual amount of Mn^{III} formed or the actual amount reduced at any instant, it is necessary to estimate the remaining persulphate or the unoxidised oxalate. An attempt was made to estimate the persulphate iodometrically by the method of Szabo, Csanyi and Galibra (*Z. anal. Chem.*, 1952, **135**, 269). It was interesting to find that no loss of persulphate could be detected even after 70 minutes. Similarly, the estimation of oxalate with permanganate showed almost no trend for the loss of oxalate. Thus, there was no loss of oxidant or reductant, although it showed visually that the red-coloured trivalent manganese was formed and passed off. A few experiments were performed with the reaction mixture covered with a layer of paraffin oil to exclude atmospheric oxidation, if any. It was found that the reaction mixture even then turned red and finally became colorless. In view of above results, it seems of importance and interest to find out how Mn^{II} is oxidised to Mn^{III}, which is subsequently reduced back to Mn^{II} without any loss of oxidant or reductant.

Experimental

As persulphate solutions are very much susceptible to variations in impurities or otherwise of the reacting solution or the nature of the glass of reaction vessels (King, *J. Amer. Chem. Soc.*, 1930, **52**, 4779 ; Allen, *ibid.*, 1951, **73**, 3589 ; Gupta and Ghosh, *Proc. Indian Sci. Cong.*, 1958, Sec. IV, Abs. No. 49), all the vessels used were of Jena glass and redistilled water from a quartz vessel was the medium of reaction. All the chemicals were of B.D.H.-A.R. quality.

FIG. 1

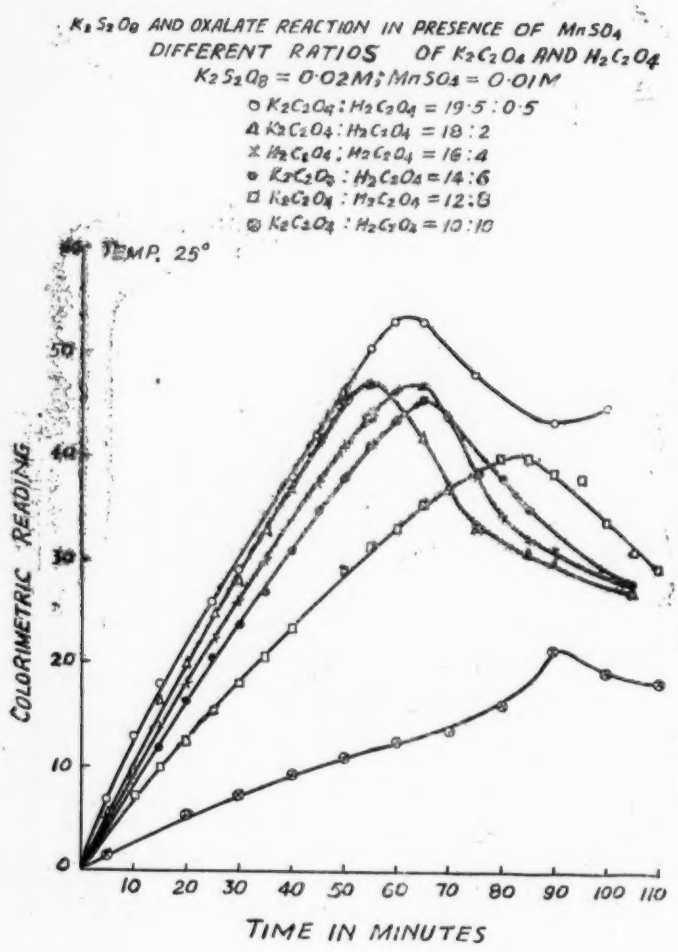
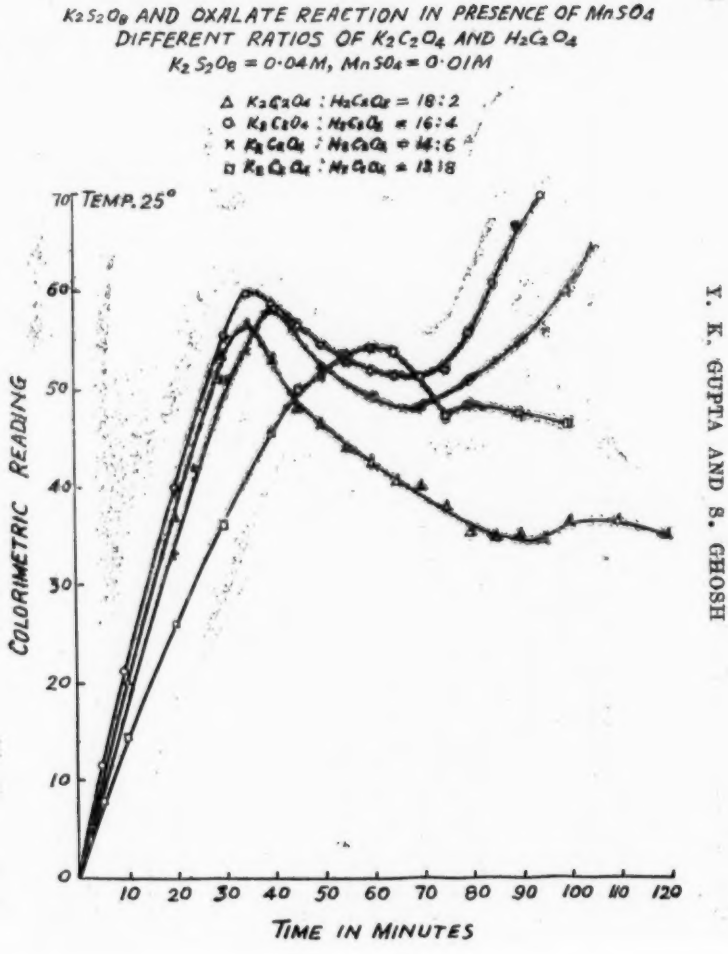

$K_2S_2O_8$ AND OXALATE REACTION IN PRESENCE OF $MnSO_4$
DIFFERENT RATIOS OF $K_2C_2O_4$ AND $H_2C_2O_4$
$K_2S_2O_8 = 0{\cdot}02M$; $MnSO_4 = 0{\cdot}01M$
○ $K_2C_2O_4 : H_2C_2O_4 = 19{\cdot}5 : 0{\cdot}5$
△ $K_2C_2O_4 : H_2C_2O_4 = 18 : 2$
× $K_2C_2O_4 : H_2C_2O_4 = 16 : 4$
● $K_2C_2O_4 : H_2C_2O_4 = 14 : 6$
□ $K_2C_2O_4 : H_2C_2O_4 = 12 : 8$
⊗ $K_2C_2O_4 : H_2C_2O_4 = 10 : 10$
TEMP. 25°
COLORIMETRIC READING
0 10 20 30 40 50
10 20 30 40 50 60 70 80 90 100 110
TIME IN MINUTES

FIG. 2


$K_2S_2O_8$ AND OXALATE REACTION IN PRESENCE OF $MnSO_4$
DIFFERENT RATIOS OF $K_2C_2O_4$ AND $H_2C_2O_4$
$K_2S_2O_8 = 0{\cdot}04M$, $MnSO_4 = 0{\cdot}01M$
△ $K_2C_2O_4 : H_2C_2O_4 = 18 : 2$
○ $K_2C_2O_4 : H_2C_2O_4 = 16 : 4$
× $K_2C_2O_4 : H_2C_2O_4 = 14 : 6$
□ $K_2C_2O_4 : H_2C_2O_4 = 12 : 8$
TEMP. 25°
COLORIMETRIC READING
0 10 20 30 40 50 60 70
10 20 30 40 50 60 70 80 90 100 110 120
TIME IN MINUTES

Known amounts of persulphate, potassium oxalate and oxalic acid were taken in the reaction vessel and put in a thermostat at 25°. Calculated quantity of $MnSO_4$ at the same temperature was added to the reaction vessel. At suitable intervals of time, a portion of the reaction mixture was taken out and the red-coloured compound appearing in the system was determined by a Klett-Summerson photoelectric colorimeter, using filter No. 50. A preliminary spectrophotometric study of the reaction mixture with different ratios of potassium oxalate and oxalic acid showed maximum absorption at different wave-lengths in the range of 480-510 mμ. The choice of filter No. 50 was arbitrary in view of the maximum absorption of the red-coloured $Mn_2(SO_4)_3$, being at 505 mμ (Gupta and Ghosh, *Naturwiss.*, 1958, **45**, 184). This does not matter in our investigations because where the results have been compared, the ratio of potassium oxalate to oxalic acid is same. $K_2S_2O_8$ or $MnSO_4$ showed no absorption for filter No. 50.

Discussion

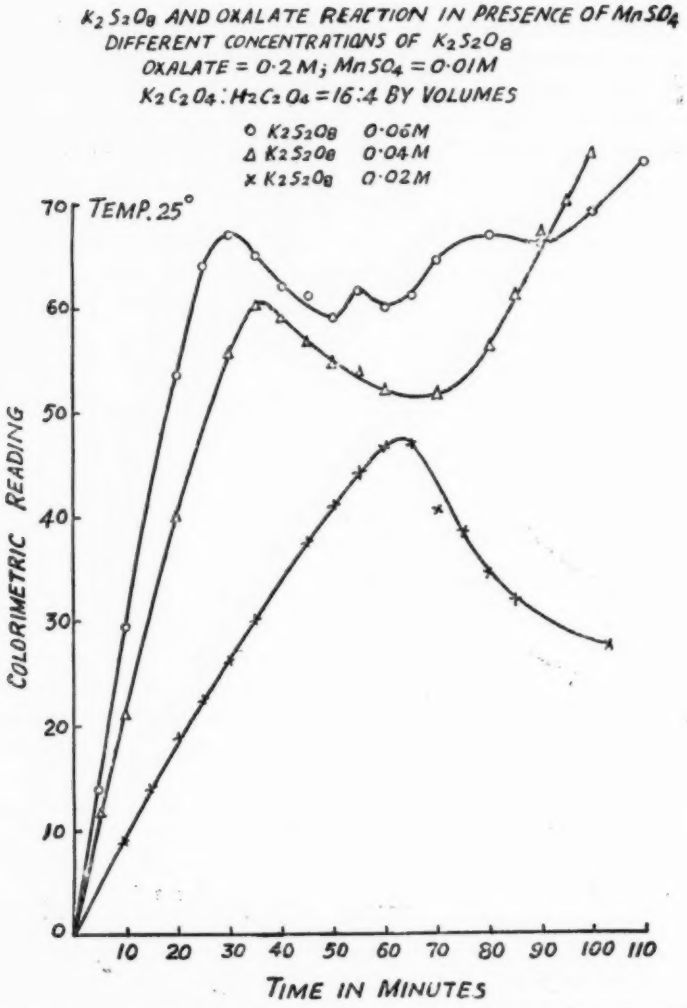
Figs. 1 to 5 represent some of the readings of the colorimeter for the different concentrations of persulphate, manganous sulphate and different proportions of potassium oxalate and oxalic acid.

The colorimetric readings increase with the increase in the concentrations of persulphate and manganous sulphate. This, of course, is true only of the initial readings till the maximum is reached. With increasing proportion of oxalic acid, readings at any instant decrease because of dissociation of the red trioxalate complex into dioxalate complex (Gupta and Ghosh, *Z. physikal. Chem.*, 1958, **208**, 368).

It will be seen from the figures that the colorimetric readings pass through a maximum, but again rise in most cases. In a few cases the readings are more than even what they are at maximum. It seems that in the later stages of the reaction, atomspheric oxygen oxidises Mn^{II} with the help of some reaction product formed in the system or that bivalent manganese obtained by the reduction of Mn^{III} is in a favourable or an activated state to be easily oxidised by the atmospheric oxygen. The latter suggestion in the present circumstances seems to be more probable.

In our kinetic expreriments no precipitate of manganous oxalate was obtained on mixing manganous sulphate and the oxalate. A slight precipitate, the amount depending on the concentration of Mn^{II}, however, did appear after about 2 to 3 hours. Also, a mixture of manganous sulphate and the oxalate of the concentrations used in the present investigation, did not afford a precipitate of manganous oxalate even after 24 hours. It appears from the above results that Mn^{II}, obtained by the reduction of Mn^{III}, behaves differently from the one obtained from the manganous sulphate solution. The former is capable of being oxidised by the atmospheric oxygen and it can easily form a precipitate of manganous oxalate.

FIG. 3



The colorimetric readings increase with the increase in the concentrations of persulphate and manganous sulphate. Hence, the slow step involves both the persulphate and the Mn^{2+} ions. This is a single instance in persulphate oxidation reactions where the rate depends on the concentration of the reductant also. The uncatalysed oxidation of Mn^{II} by persulphate is very slow (Gupta and Ghosh, unpublished). No Mn^{III} or MnO_2 is ordinarily obtained, but in presence of oxalate, oxidation to Mn^{III} does take place where Mn^{III} is present in the form of oxalate complexes. It appears therefore that Mn^{II} as such is not oxidised by persulphate whereas Mn^{II} as oxalate complex is probably oxidised. The following mechanism may now be suggested for the appearance and disappearance of the red colour.

$$S_2O_8^{2-} \rightleftharpoons SO_4^{2-} + SO_4 \quad \ldots \text{ slow } (1)$$

$$Mn(C_2O_4)_2^{2-} + SO_4 \rightleftharpoons Mn(C_2O_4)_2^{-} + SO_4^{-} \quad \ldots \text{ slow } (2)$$

$$Mn(C_2O_4)_2^{-} + C_2O_4^{2-} \rightleftharpoons Mn(C_2O_4)_3^{3-} \quad \ldots \text{ rapid } (3)$$

$$Mn(C_2O_4)_2^{-} \rightleftharpoons Mn^{3+} + 2C_2O_4^{2-} \quad \ldots \text{ rapid } (4)$$

$$Mn^{3+} + H_2O \rightleftharpoons Mn^{2+} + H^+ + OH \quad \ldots \text{ slow } (5)$$

$$SO_4^{-} + OH \rightleftharpoons HSO_5^{-} \quad \ldots \text{ fast } (6)$$

Step (1) is based on the mechanism suggested by the authors for the uncatalysed oxidation of arsenious acid by persulphate (Gupta and Ghosh, *loc. cit.*). Step (2) is the oxidation of Mn^{II} which is slow because the colorimetric readings depend on the concentration of manganous sulphate also. Steps (3) and (4) are well known. Step (5) has been confirmed in this laboratory by Chakravarti and Ghosh (*Z. physikal. Chem.*, 1957, **207**, 392). In the oxidation of oxalate by Mn^{III}, the radical OH is responsible for oxidation, which in the present case is co-ordinated to SO_4^- to form Caro's acid, and thus oxalate is not oxidised. Small amounts of H_2O_2 from Caro's acid are also produced.

FIG. 4

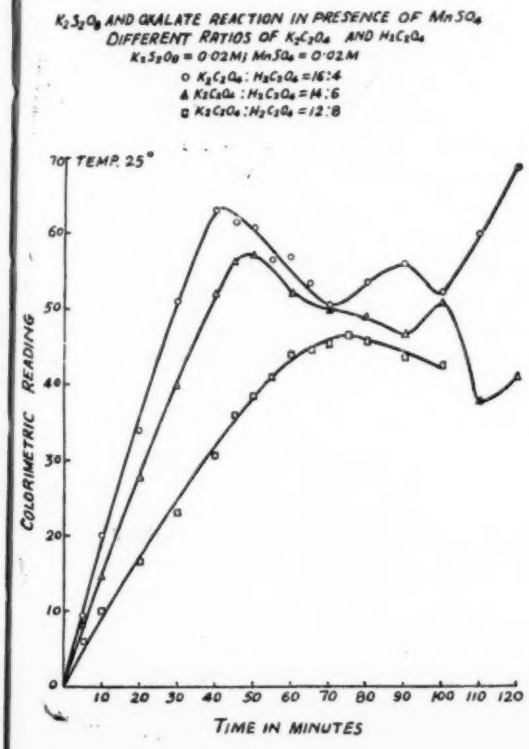
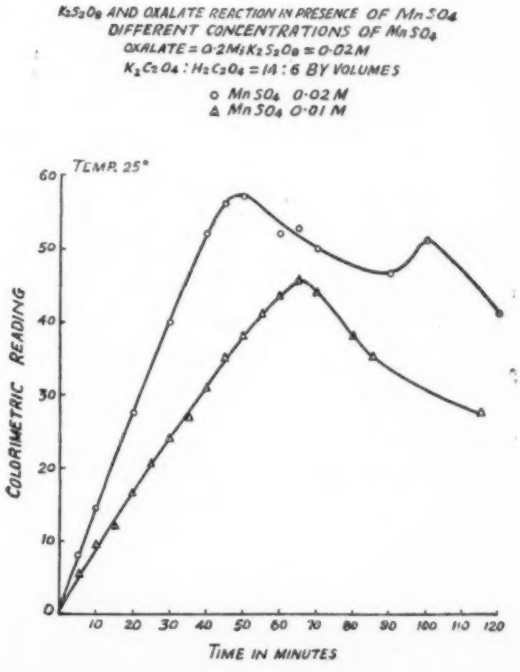

K2S2O8 AND OXALATE REACTION IN PRESENCE OF MnSO4
DIFFERENT RATIOS OF K2C2O4 AND H2C2O4
K2S2O8 = 0·02M; MnSO4 = 0·02M
○ K2C2O4 : H2C2O4 = 16:4
△ K2C2O4 : H2C2O4 = 14:6
□ K2C2O4 : H2C2O4 = 12:8
TEMP. 25°
COLORIMETRIC READING
TIME IN MINUTES

FIG. 5


K2S2O8 AND OXALATE REACTION IN PRESENCE OF MnSO4
DIFFERENT CONCENTRATIONS OF MnSO4
OXALATE = 0·2M; K2S2O8 = 0·02M
K2C2O4 : H2C2O4 = 14 : 6 BY VOLUMES
○ MnSO4 0·02M
△ MnSO4 0·01M
TEMP. 25°
COLORIMETRIC READING
TIME IN MINUTES

No direct evidence for the existence of H_2SO_5 could be provided in the presence of persulphate and H_2O_2 except for the fact that it liberates iodine from KI much quicker than persulphate or H_2O_2. In the following experiments the reactants were mixed in the test tubes and allowed to react for 24 hours. Dilute H_2SO_4 (1 c.c.) and dilute KI (5 c.c.) were then added to all the test tubes quickly one after the other.

TABLE I

Expt. No.	$K_2S_2O_8$ (0.1 *M*).	$MnSO_4$ (0.2 *M*).	$K_2C_2O_4$ (0.1 *M*).	$H_2C_2O_4$ (0.1 *M*).	H_2O.
1	8 c.c.	...	...	...	12 c.c.
2	8	...	7 c.c.	1 c.c.	4
3	8	1 c.c.	7	1	3

It was seen that in expt. 3, where both manganous sulphate and oxalate were present, visually more of iodine was liberated in a definite time, probably due to the formation of Caro's acid. Similarly, the oxidation of oxalate by Mn^{III} was found to slow down in presence of persulphate and manganous sulphate. This indirectly supports the view that OH radicals (obtained through step 5 of the mechanism) are co-ordinated to SO_4^- (obtained through the oxidation of Mn^{II} oxalate complexes by persulphate) to form Caro's acid which does not oxidise oxalate or Mn^{II}.

We have found (unpublished) the anticatalytic action of Mn^{II} in the silver-catalysed oxidation of oxalate by persulphate. Similarly we have observed that the silver-catalysed oxidation of Mn^{II} by persulphate, which ordinarily gives MnO_2, is slowed down in acid medium. The kinetics were followed by dissolving MnO_2 in a known excess of oxalic acid and estimating the unused oxalic acid with $KMnO_4$. High estimated values of unused oxalate were obtained. In acid medium stable Mn^{III} is formed and this on reduction gives OH which is co-ordinated with SO_4^- available from the persulphate. Thus, oxalate is not oxidised. Hence, the oxidation of Mn^{II}, in fact, is not slowed down, but that the method of following the kinetics is no more suitable in acid medium in presence of persulphate. All the above facts indirectly support our views regarding the formation of Caro's acid in the mechanism suggested.

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CHEMICAL EXAMINATION OF THE LEAVES OF *CLITORIA TERNATEA* LINN

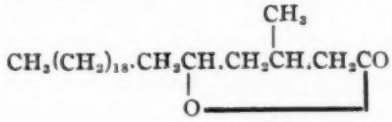
By R. D. Tiwari and R. K. Gupta *

From the alcoholic extract of the dried leaves of *Clitoria ternatea*, Linn., belonging to the N. O. Leguminosae, a δ-lactone, aparajitin (m.p. 92-93°) having the molecular formula $C_{26}H_{50}O_2$ has been isolated. From its oxidation products, arachidic acid and β-methylglutaric acid, aparajitin has been found to be a δ-lactone of 2-methyl-4 hydroxy-*n*-pentacosanoic acid.

Clitoria ternatea Linn (commonly known as *Aparajita*), belonging to the *Papilionaceae* sub-group of the Leguminosae family, is a perennial twining herb, commonly found all over India. Practically all parts of the plant including leaves are reported to possess medicinal properties. (Basu and Kirtikar, "Indian Medicinal Plants", Vol. I, p. 689).

No systematic chemical examination of the plant has so far been reported but for the fact that the seeds are known to contain a fixed oil and a bitter resinous principle (Dymock, Warden and Hooper, "Pharmacographica Indica", Vol. I, p. 460). A systematic chemical examination of the various parts of the plant has been made and the results of the examination of the leaves of the blue flowered variety of the plant are reported herein.

The alcoholic extract of the dried leaves deposited, on keeping, a white flocculent solid, which on crystallisation from alcohol provided a white amorphous powder, m.p. 92-93°. This compound has been found to be a lactone, $C_{26}H_{50}O_2$, which we have provisionally named "aparajitin". On boiling with hydrobromic acid and hydroiodic acid respectively, it gave $C_{26}H_{51}O_2Br$ and $C_{26}H_{51}O_2I$. These halogen compounds are found to be 2-methyl-4-bromo- and 2-methyl-4-iodo-*n*-pentacosanoic acids. On esterification it furnished a compound, $C_{27}H_{54}O_3$, which was found to undergo acetylation, suggesting it to be an ester of a hydroxy-acid. Aparajitin is *laevo*-rotatory. On oxidation with potassium permanganate, chromic acid or nitric acid, it gives rise in each case to a monobasic acid (A), m.p. 75°, found identical with arachidic acid, and a dibasic acid (B), m.p. 83-84°, identical with β-methylglutaric acid. On the basis of all these experimental results the lactone has been assigned the following structure :



(I)

This is in agreement with the fact that whereas the original compound is optically active, neither of the two acids obtained by its degradation shows any optical activity.

Experimental

The leaves of the plant *Clitoria ternatea* for the purpose of chemical examination were obtained from the Punjab Ayurvedic Pharmacy, Amritsar and identified locally.

Present address: National Botanical Gardens, Lucknow.

The powdered leaves (5 kg.) were exhaustively extracted with alcohol in several instalments. The alcoholic extract on cooling deposited a white flocculent mass (0.14%) which was filtered off. The dark green filtrate after concentration to about one fourth of the original volume was kept overnight, when a little more of the residue was obtained.

Isolation of Aparajitin.—The residue, obtained as above, was boiled with a large excess of alcohol and filtered hot. The filtrate on keeping deposited a white clear mass. The process was repeated twice when the residue obtained was practically white. Finally the product was refluxed with alcohol and a little of animal charcoal and filtered hot. The filtrate now deposited a clear white residue, m.p. 92–93°. It was dried over calcium chloride in a vacuum desiccator. The melting point did not rise on further crystallisations and also the mixed melting point of the two fractions on subsequent crystallisations remained unaltered. In order to confirm the purity of the product, spots of aparajitin in benzene solution were put on strips of Whatman No. 1 filter paper and it was run on *n*-butanol-acetic acid-water (4 : 1 : 5) for 24 hours. The chromatograms were developed with 1% benzidine phthalate solution in alcohol. In each case only one spot was obtained.

Properties of Aparajitin.—The compound is insoluble in water, cold alcohol, chloroform, ether and petroleum ether ; sparingly soluble in acetone and soluble in hot alcohol, benzene, ethyl acetate and pyridine. The compound also dissolves in alkali and from the solution the original compound is precipitated back on addition of mineral acid. It does not decolorise bromine water or alkaline potassium permanganate solution and affords no acetyl derivative. It does not reduce Fehling's solution nor responds to any test for a keto group. The compound is *laevo*-rotatory. [Found : C, 79.01 ; H, 12.86 ; M.W. (Rast), 391. $C_{26}H_{50}O_2$ requires C, 79.18 ; H, 12.69% ; M.W. 394].

Action of Hydroiodic Acid on Aparajitin.—The compound (1 g.) was refluxed with 10. c.c. of freshly distilled hydroiodic acid, b.p. 127°, for 6 hours. The contents were poured in water with constant stirring. The precipitated mass was filtered and washed well first with 2% sodium thiosulphate solution to remove the adhering iodine and finally with distilled water. The residue was crystallised from hot alcohol when an ash-coloured amorphous product, melting at 68°, was obtained. (Found : I, 24.01. $C_{26}H_{51}O_2I$ requires I, 24.33%).

Action of Hydrobromic Acid on Aparajitin.—The compound (1 g.) was refluxed with HBr (20 c.c.) for 4 hours. The reaction mixture was poured in water, filtered and washed well with 5% sodium thiosulphate solution to remove the excess of bromine and finally with distilled water. The bromo derivative was crystallised from hot acetone, m.p. 81°, remaining unchanged on further crystallisations. It is soluble in benzene, ether, chloroform and carbon tetrachloride and insoluble in water. (Found : Br, 16.64. $C_{26}H_{51}O_2Br$ requires Br, 16.84%).

Esterification of Aparajitin.—The compound (1 g.), freshly distilled methyl alcohol (10 c.c.) and H_2SO_4 (conc., 1 c.c.) were refluxed on a water-bath for 10 hours. The excess of methyl alcohol was distilled off. After cooling, the product was poured in water with constant stirring. The semisolid mass was extracted with ether and the ethereal layer was washed well with water to remove the adhering sulphuric acid. The

methyl ester was crystallised from hot acetone as a white amorphous product, m.p. 74°. It is soluble in ether and chloroform and insoluble in water, benzene and pyridine. (Found : C, 75.95 ; H, 12.34. $C_{27}H_{54}O_3$ requires C, 76.21 ; H, 12.64%).

Acetylation of the Ester of Aparajitin.—The above methyl ester (0.50 g.) was mixed with fused sodium acetate (1 g.) and acetic anhydride (4 c.c.) and refluxed for 4 hours. The contents were poured in water with constant stirring. The acetylated ester was crystallised from hot alcohol as a white amorphous powder, m.p. 71°. (Found : C, 74.31 ; H, 11.72 ; OAc, 9.20. $C_{29}H_{56}O_4$ requires C, 74.53 ; H, 11.90 ; OAc, 9.18%).

Oxidation Products of Aparajitin.—Aparajitin (2 g.) was taken in a 200 c.c. conical flask and HNO_3 (70% w/w, 15 c.c.) was added to it. The acid reacted vigorously, evolving dense fumes of nitrogen peroxide at room temperature. When the fumes had subsided, the flask was heated on a water-bath for 3 hours with occasional shaking. The reaction mixture was poured in water (15 c.c.). The precipitated fatty acid (A) was filtered and washed with water till the washings were non-acidic to methyl orange. The filtrate and the washings were evaporated to dryness on a water-bath and the residue was extracted with ether, when a dibasic acid (B) was obtained.

Acid (A).—The fatty acid obtained as above was crystallised from dilute acetone, m.p. 75° ; the m.p. did not rise on subsequent crystallisations. (Found : C, 77.12 ; H, 12.68 ; M.W. 314.5. Calc. for $C_{20}H_{40}O_2$: C, 76.92 ; H, 12.82% ; M.W. 312).

The acid was identified as arachidic acid ; mixed m.p. with an authentic sample of arachidic acid remained undepressed.

Acid (B).—The dibasic acid obtained as above melted at 84°. The acid gave fluorescein test and was optically inactive. (Found : C, 49.67 ; H, 6.94 ; M.W. 145.3. Calc. for $C_6H_{10}O_4$: C, 49.33 ; H, 6.86% ; M.W. 146).

The mixed m.p. of the acid gave no depression with pure β-methylglutaric acid. Further, β-methylglutaric acid should be optically active but not the α-.

Oxidation of aparajitin was done with chromic acid and also with alkaline $KMnO_4$ solution. The products of oxidation in each case were arachidic acid and β-methylglutaric acid, similar to those obtained by nitric acid oxidation.

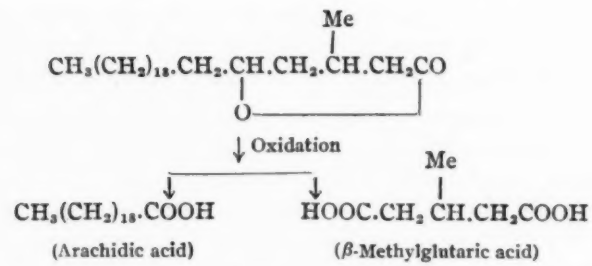
Constitution of Aparajitin

On the basis of the above experiments, it becomes clear that aparajitin is a δ-lactone of the structure (I) (*vide supra*).

On treatment with hydroiodic acid and hydrobromic acid respectively, it furnished 2-methyl-4-iodo-*n*-pentacosanoic acid, $C_{26}H_{51}O_2I$, and 2-methyl 4-bromo-*n*-pentacosanoic acid, $C_{26}H_{51}O_2Br$.

On esterification, aparajitin gave the methyl ester of 2-methyl-4-hydroxy-*n*-pentacosanoic acid, which formed an acetyl derivative of 2-methyl 4-hydroxymethyl-*n*-pentacosanoate.

The formation of arachidic acid and β-methylglutaric acid by oxidation could be explained as shown below.



The reactions of aparajitin with hydrobromic acid, hydroiodic acid and methyl alcohol are comparatively slow, suggesting a δ-lactone structure in preference to the γ-lactone. This is further confirmed by the nature of the dibasic acid obtained by oxidation of aparajitin which has been found to be a derivative of glutaric acid and not of succinic acid.

The authors wish to make a grateful acknowledgement to the Govt. of India for a senior scholarship to one of them (R.K.G.) which enabled him to take part in the present work and to the University of Allahabad for providing research facilities.

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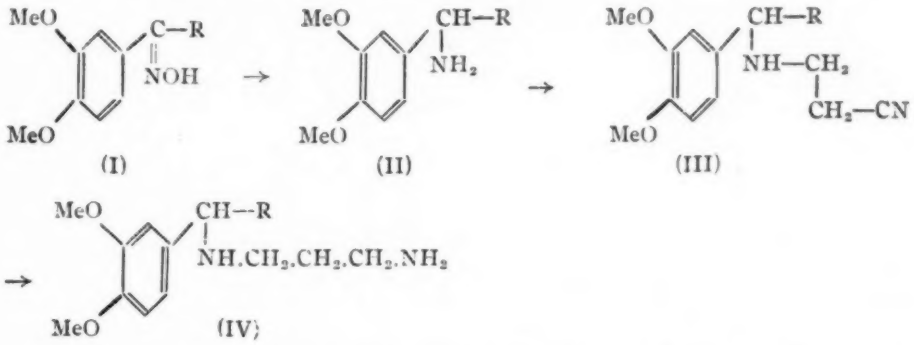
SYNTHESIS OF POSSIBLE AMOEBACIDES. PART III

By H. N. Sharma and C. N. Kachru

Synthesis of 1-(4′-veratryl)-(*N*-γ-aminopropyl$^{\alpha}$)-alkylamines with alkyl groups such as, ethyl, propyl$^{\alpha}$ and butyl$^{\alpha}$, has been achieved by the following steps: 1-(4′-veratryl)-alkylamine → 1-(4′-veratryl)-(*N*-cyanoethyl)-alkylamine → 1-(4′-veratryl)-(*N*-γ-aminopropyl$^{\alpha}$)-alkylamine.

Hall *et al.* (*J. Chem. Soc.*, 1950, 1842; 1952, 149) and Mahboob and Dhar (*J. Sci. Ind. Res.*, 1955, **14B**, 1) have synthesised several diamines in the search for a substitute of emetine in amoebiasis. None of these compounds showed any superiority to emetine *in vivo*. The object of the present investigation is to synthesise 1-(4′-veratryl)-*N*-(γ-aminopropyl$^{\alpha}$)-alkylamines with alkyl groups such as, ethyl, propyl$^{\alpha}$ and butyl$^{\alpha}$, so that these may be tested for amoebacidal activity.

These compounds have been synthesised by the route shown below:



Acylveratroles (Kachru and Pathak, this *Journal*, 1957, **34**, 611) were converted into the corresponding oximes (I) in the usual way, which on subsequent reduction with sodium and absolute alcohol yielded 1-(4′-veratryl)-alkylamines (II). These were condensed with acrylonitrile to form the cyanoethyl products (III). Subsequent reduction to compounds of the type (IV) was achieved with lithium aluminium hydride.

Experimental

1-(4′-Veratryl)-ethylamine (II: R = Me).—In a 500 c.c. two-necked flask provided with a reflux condenser and a KOH guard tube were introduced acetoveratrone oxime (Pictet and Gams, *Ber.*, 1900, **42**, 2947; 11 g.) and absolute alcohol (100 c.c.) and the mixture was heated on a water-bath till alcohol commenced refluxing. Heating was then discontinued and sodium (15 g.) was added to the reaction mixture as rapidly as possible, 100 c.c. more of absolute alcohol being added to maintain a vigorous reaction. Towards the end, the flask was heated in order to dissolve the last traces of sodium. The flask was cooled and the content decomposed by HCl. Alcohol was removed by

distillation under reduced pressure. The residue was triturated with water. Any unchanged oxime was removed by extraction with benzene. The aqueous layer was then made alkaline with KOH solution and the separated amine was extracted with benzene. The benzene solution was dried over KOH and the amine distilled, b.p. 120°/1 mm, yield 7 g. (68.5%). The *picrate* was crystallised from water in golden yellow crystals, m.p. 125°. The *hydroiodide* melted at 212°. Its *hydrochloride* was crystallised from a mixture of absolute alcohol and ethyl acetate, m.p. 214°. (Found: N, 6.38. $C_{10}H_{16}O_2NCl$ requires N, 6.43%).

1-(4′-*Veratryl*)-(N-*cyanoethyl*)-*ethylamine* (III: R = Me).—Acrylonitrile (2.5 g.) was added dropwise with stirring during the course of 2 hours to 1-(4′-veratryl)-ethylamine (10.7 g.), the temperature being kept below 30°. Stirring was continued for 5 hours after the addition was complete and the mass left overnight. The mixture was then refluxed on the steam-bath for 15 minutes. Vacuum distillation of the mixture yielded 8.6 g. (62%) of the cyanoethyl product (b.p. 183-85°/1 mm) and 2.7 g. of the unchanged amine. The *picrate* was crystallised from hot water in golden yellow crystals, m.p. 155°. The *hydroiodide* melted at 165°. The *hydrochloride* was crystallised from a mixture of absolute alcohol and ethyl acetate, m.p. 167°. (Found: N, 10.52. $C_{13}H_{19}O_2N_2Cl$ requires N, 10.35%).

1-(4′-*Veratryl*)-(N-γ-*aminopropyl**)-*ethylamine* (IV: R = Me).—1-(4′-Veratryl)-(N-cyanoethyl)-ethylamine (5.9 g.), dissolved in anhydrous ether, was added portionwise to a slurry of $LiAlH_4$ (1.5 g.) and anhydrous ether (200 c.c.). After the vigorous reaction had subsided, the reaction mass was gently refluxed for 2 hours and then left overnight. Next day the excess of $LiAlH_4$ was decomposed by dropwise addition of water. The ethereal layer was separated and dried over KOH. The ether was removed and the diamine distilled off, b.p. 140°/1mm, yield 2.3 g. (38.3%). The *picrate* was crystallised from alcohol, m.p. 163°. The *hydrochloride* was crystallised from ethyl acetate, m.p. 207°. (Found: C, 50.01; H, 7.61; N, 9.11. $C_{13}H_{24}O_2N_2Cl_2$ requires C, 50.16; H, 7.71; N, 9.00%).

(4′-*Veratryl*)-*ethyl Ketoxime* (I: R = Et).—4′-Veratrylethyl ketone (Kachru and Pathak, *loc. cit.*, 25 g.), hydroxylamine hydrochloride (35 g.) and sodium acetate (65 g.) were dissolved in aqueous alcohol and refluxed for 1 hour. It was then cooled when the oxime separated as a viscous oil which solidified on long standing. It was crystallised from dilute alcohol, m.p. 66°. (Found: N, 6.72. $C_{11}H_{15}O_3N$ requires N, 6.69%).

1-(4′-*Veratryl*)-*propylamine** (II: R = Et).—The above oxime, prepared from the corresponding ketone (25 g.), was reduced with metallic sodium (28 g.) and absolute alcohol (250 c.c.) in the usual manner, as described under compound (II: R = Me). The amine distilled at 124-25°/1 mm, yield 12 g. (47.7% as calculated on the basis of the ketone). The *picrate* was crystallised from hot water as yellow prisms, m.p. 180°. The *hydrochloride* was crystallised from a mixture of absolute alcohol and ethyl acetate as white shining flakes, m. p. 238° (decomp.). (Found: N, 6.12. $C_{11}H_{18}O_2NCl$ requires N, 6.05%).

1-(4′-*Veratryl*)-(N-*cyanoethyl*)-*propylamine** (III: R = Et).—Acrylonitrile (2.3 g.) was added dropwise with stirring to the above amine (9.3 g.) during the course of

2 hours. The rest of the procedure was the same as described under (III : R = Me). The cyanoethyl product distilled at 170-75°/1 mm, yield 6.35 g. (53.7%). The *picrate* was crystallised from hot water as golden yellow needles, m.p. 160°. The *hydrochloride* was crystallised from a mixture of absolute alcohol and ethyl acetate as colorless needles, m.p. 234-35° (decomp.). (Found : N, 9.92. $C_{14}H_{21}O_2N_2Cl$ requires N, 9.84%).

1-(4′-*Veratryl*) - (N-γ-*aminopropyl*^{n})-*propylamine*^{n} (IV : R = Et).—The preceding amine (III : R = Et ; 5 g.) was reduced by $LiAlH_4$ (1.28 g.) using anhydrous ether (100 c.c.) as a solvent in the manner described under (IV : R = Me). The diamine distilled at 132-35°/1 mm, yield 2.5 g. (49%). The *picrate* was crystallised from hot water as dark yellow flakes, m.p. 99°. The *hydrochloride* was crystallised from a mixture of ethyl acetate and absolute alcohol in white shining flakes, m.p. 229° (decomp). (Found : C, 51.80 ; H, 8.20 ; N, 8.62. $C_{14}H_{26}O_2N_2Cl_2$ requires C, 51.69 ; H, 8.00 ; N, 8.61%).

(4′-*Veratryl*)-*propyl*^{n} *Ketoxime* (I : R = Pr^n).—4′-Veratryl^n propyl ketone (Kachru and Pathak, *loc. cit.* ; 23 g.), hydroxylamine hydrochloride (30 g.) and crystallised sodium acetate (60 g.), dissolved in aqueous alcohol, were refluxed for 1 hour. The product was cooled, when the oxime separated as a brown viscous oil which was extracted with ether. The ether extract was dried and the ether removed. The residual liquid was subjected to reduction to the corresponding amine as such.

1-(4′-*Veratryl*)-*butylamine*^{n} (II : R = Pr^n).—The above oxime was reduced by metallic sodium (28 g.) and absolute alcohol (250 c.c.) in the usual manner as described before. The amine distilled at 130-35°/1 mm, yield 8.7 g. (38% on the basis of ketone). The *picrate* was crystallised from dilute alcohol as bright yellow needles, m.p. 187°. The *hydrochloride* was crystallised from a mixture of absolute alcohol and ethyl acetate in colorless prisms, m.p. 227° (decomp.). (Found : N, 5.81. $C_{12}H_{20}O_2NCl$ requires N, 5.70%).

1-(4′-*Veratry*)-(N-*cyanoethyl*)-*butylamine*^{n} (III : R = Pr^n).—The procedure adopted was the same as used in the preparation of (III : R = Me) using the above amine (7.3 g.) and acrylonitrile (1.6 g.). The cyanoethyl product distilled at 158-60°/1 mm, yield 5.9 g. (64.5%). The *picrate* was crystallised from dilute alcohol as yellow needles, m.p. 161°. The *hydrochloride* was crystallised from a mixture of absolute alcohol and ethyl acetate as white prisms, m.p. 220°. (Found : N, 9.45. $C_{15}H_{23}O_2N_2Cl$ requires N, 9.38%).

1-(4′-*Veratryl*)-(N-γ-*aminopropyl*^{n})-*butylamine*^{n} (IV : R = Pr^n).—The above cyanoethyl product (4.1 g.) was reduced with $LiAlH_4$ (1.0 g.) and anhydrous ether as a solvent according to the procedure indicated under compound (IV : R = Me). The diamine was extracted with ether and converted into the hydrochloride. The *hydrochloride* was crystallised from a mixture of ethyl acetate and absolute alcohol, m.p. 212°, yield 3.5 g. (66%). (Found : C, 53.32 ; H, 8.31 ; N, 8.32. $C_{15}H_{28}O_2N_2Cl_2$ requires C, 53.1 ; H, 8.26 ; N, 8.26%). The *picrate* was crystallised from dilute alcohol in bright yellow needles, m.p. 169°.

The authors express their sincere thanks to Dr. Mata Prasad, Vice-Chancellor, Vikram University, for providing research facilities and to Dr. B. Pathak of the Department of Applied Chemistry, Calcutta University, for his keen interest during the course of the investigation.

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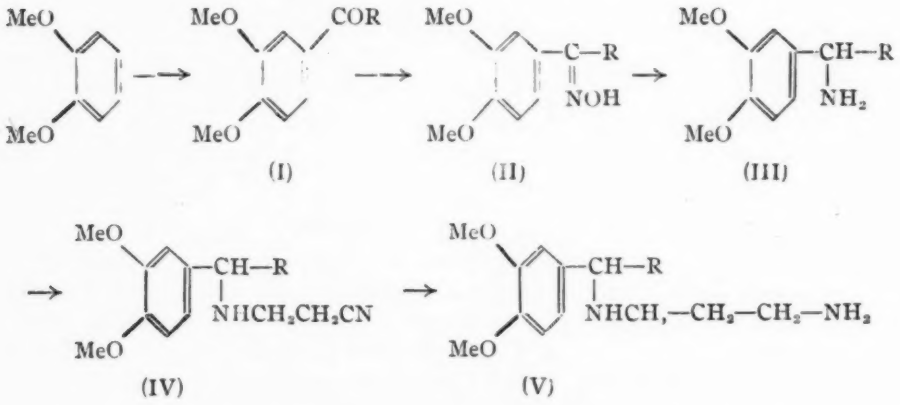
SYNTHESIS OF POSSIBLE AMOEBACIDES. PART IV

BY H. N. SHARMA AND C. N. KACHRU

1-(4′-Veratryl)-(*N*-γ-aminopropyl^n)-alkylamines, with alkyl groups such as amyl^n and hexyl^n, have been synthesised through five steps: Veratrole → 4′-veratryl-alkyl ketone → (4′-veratryl)-alkyl ketoxime → 1-(4′-veratryl)-alkylamine → 1-(4′-veratryl)-(*N*-cyanoethyl)-alkylamine → 1-(4′-veratryl)-(*N*-γ-aminopropyl^n)-alkylamine.

The work embodied in Part III (Sharma and Kachru, this *Journal*, p. 247) has been extended to the synthesis of 1-(4′-veratryl)-(*N*-γ-aminopropyl^n)-alkylamines with alkyl groups such as amyl^n and hexyl^n along the following route:



4′-Veratrylbutyl^n ketone was prepared by condensing veratrole with valeryl^n chloride in presence of anhydrous zinc chloride at the boiling temperature of CS_2. This ketone and 4′-veratrylamyl^n ketone (Kachru and Pathak, this *Journal*, 1957, **34**, 611) were converted into the corresponding oximes (II) in the usual manner, which on subsequent reduction with sodium and absolute alcohol yielded 1-(4′-veratryl)-alkylamines (III). These were condensed with acrylonitrile to form the cyanoethyl product (IV). Subsequent reduction to compound of the type (V) was achieved with lithium aluminium hydride.

EXPERIMENTAL

4′-Veratrylbutyl^n *Ketone* (I: R = $C_4H_9{}^n$).—A mixture of veratrole (120 g.), powdered anhydrous zinc chloride (120 g.), CS_2 (400 c.c.) and valeryl^n chloride (130 g.) was gently refluxed at about 60° on a water-bath for 4 hours, when HCl fumes continually evolved. A dark violet-coloured complex was formed. CS_2 was distilled off, the residual mass was decomposed by boiling with water for half an hour and the oily liquid was extracted with benzene. The benzene solution was washed successively with dilute NaOH and water, dried over anhydrous calcium chloride, and the residual oil after removal of the ether gave on distillation the ketone, b.p. 160°/1 mm, yield 100 g. (51.8%).

The ketone was a viscous liquid and did not solidify. Its *semicarbazone* was crystallised from dilute alcohol in colorless needles, m.p. 179°. (Found: N, 15.2; OMe, 22.3. $C_{14}H_{21}O_3N_3$ requires N, 15.05; OMe, 22.22%).

4′-Veratrylbutyl^n *Ketoxime* (II: R = $C_4H_9{}^n$).—4′-Veratrylbutyl^n ketone (30 g.), hydroxylamine hydrochloride (45 g.) and sodium acetate (90 g.), dissolved in aqueous alcohol, were refluxed for one hour on a water-bath. The product was cooled when the oxime separated as a viscous oil and did not solidify. It was extracted with benzene, dried over anhydrous calcium chloride and the benzene was removed by distillation. The residual liquid as such was subjected to reduction to the corresponding amine.

1-(4′-Veratryl)-amylamine^n (III: R = $C_4H_9{}^n$).—The above oxime was dissolved in dry absolute alcohol (200 c.c.) in a one litre two-necked flask equipped with a reflux condenser and a KOH guard-tube. The flask was heated on a water-bath till alcohol commenced refluxing. Heating was then discontinued and sodium (27 g.) in small pieces was added to the hot reaction mixture as rapidly as possible; 100 c.c. more of absolute alcohol was added to maintain a vigorous reaction. The reaction mixture was kept refluxing until all the sodium had dissolved. The reaction mixture was cooled and decomposed by HCl (conc.). Alcohol was removed by distillation under reduced pressure. The residue was triturated with water. Any unchanged oxime was removed by extraction with benzene. The aqueous layer was then made alkaline with KOH solution and the separated amine was extracted with benzene. The benzene solution was dried over KOH, the benzene removed and the residual amine distilled in vacuum, b.p. 130-36°/1mm, yield 14.5 g. (48.1% on the basis of ketone). The *picrate* was crystallised from dilute alcohol in bright yellow crystals, m.p. 155°. The *hydrochloride* was crystallised from a mixture of absolute alcohol and ethyl acetate in colorless needles, m.p. 221°. (Found: N, 5.5. $C_{13}H_{22}O_2NCl$ requires N, 5.39%).

1-(4′-Veratryl)-(N-cyanoethyl)-amylamine^n (IV: R = $C_4H_9{}^n$).—Acrylonitrile (2.5 g.) was added dropwise with constant stirring during the course of 3 hours to 1-(4′-veratryl)-amylamine^n (11.7 g.), the temperature being kept below 30°. Stirring was continued for 5 hours after the addition was complete and then the mixture was left

overnight. The mixture was then refluxed on the steam-bath for 15 minutes and on distillation under vacuum it gave the colorless cyanoethyl product, b.p. 155-65°/1 mm, yield 8.3 g. (57.3%) and 3.1 g. of unchanged amine. The *picrate* was crystallised from dilute alcohol in yellow needles, m.p. 150°. The *hydrochloride* was crystallised from a mixture of absolute alcohol and ethyl acetate, m.p. 216°. (Found : N, 9.1. $C_{16}H_{23}O_2N_2Cl$ requires N, 8.96%).

1-(4′-*Veratryl*)-(N-γ-*aminopropyl*ⁿ)-*amylamine*ⁿ (V : R = C_4H_9ⁿ).—The preceding amine (IV : R=Buⁿ) (5.8 g.), dissolved in anhydrous ether, was added portionwise to a slurry of $LiAlH_4$ (1.2 g.) and anhydrous ether (200 c.c.). After the vigorous reaction had subsided, the reaction flask was gently refluxed for 2 hours and then left overnight. Next day the excess of $LiAlH_4$ was decomposed by dropwise addition of water. The ethereal layer was separated and dried over KOH. The ether was removed and the diamine was distilled under vacuum, b.p. 145°/1 mm, yield 2.45 g. (41.6%). The *picrate* was crystallised from dilute alcohol in brown-yellow crystals, m.p. 162°. The *hydrochloride* was crystallised from ethyl acetate, m.p. 218°. (Found : C, 54.42 ; H, 8.34 ; N, 7.84. $C_{16}H_{30}O_2N_2Cl_2$ requires C, 54.39 ; H, 8.5 ; N, 7.9%).

(4′-*Veratryl*)-*amyl*ⁿ *Ketoxime* (II : R=C_5H_{11}ⁿ).—4′-Veratrylamylⁿ ketone (Kachru and Pathak, this *Journal*, 1957, **34**, 611) (30 g.), hydroxylamine hydrochloride (45 g.) and crystallised sodium acetate (90 g.), dissolved in aqueous alcohol, were refluxed for 1 hour. The product was cooled, when the oxime separated as a viscous oil which was extracted with benzene. The benzene extract was dried and then distilled to remove benzene. The residual liquid oxime, since it did not solidify, was subjected to reduction to the corresponding amine as such.

1-(4′-*Veratryl*)-*hexylamine*ⁿ (III : R=C_5H_{11}ⁿ).—The above oxime was reduced by metallic sodium (27 g.) and absolute alcohol (300 c.c.) in the usual manner as described in the preparation of (III : R=C_4H_9ⁿ). The amine distilled at 140°/1 mm, yield 15.5 g. (51.4% on the basis of ketone). The *picrate* was crystallised from dilute alcohol in bright yellow crystals, m.p. 155°. The *hydrochloride* was crystallised from a mixture of absolute alcohol and ethyl acetate in colorless prisms, m.p. 228°. (Found : N, 5.2. $C_{14}H_{24}O_2NCl$ requires N, 5.12%).

1-(4′-*Veratryl*)-(N-*cyanoethyl*)-*hexylamine*ⁿ (IV : R=C_5H_{11}ⁿ).—Acrylonitrile (2.4 g.) was added dropwise with constant stirring to the above amine (12 g.) during the course of 3 hours. The rest of the procedure was the same as described under (IV : R=C_4H_9ⁿ). The cyanoethyl product distilled under vacuum at 165-70°/1 mm, yield 7.8 g. (53.1%). The *picrate* was crystallised from dilute alcohol in bright yellow crystals, m.p. 170°. The *hydrochloride* was crystallised from a mixture of absolute alcohol and ethyl acetate in white prisms, m.p. 223°. (Found : N, 8.63. $C_{17}H_{27}O_2N_2Cl$ requires N, 8.58%).

1-(4′-*Veratryl*)-(N-γ-*aminopropyl*ⁿ)-*hexylamine*ⁿ (V : R=C_5H_{11}ⁿ).—The preceding hexylamine (5.9 g.) was reduced by $LiAlH_4$ (1.2 g.) using anhydrous ether (200 c.c.) as a solvent. The procedure adopted was the same as used in the preparation of

(V: R=$C_4H_9^n$). The diamine distilled under vacuum, b.p. 145-50°/1 mm, yield 2.4 g. (40.1%). The *picrate* was crystallised from dilute alcohol in yellow needles, m.p. 165°. The *hydrochloride* was crystallised from a mixture of ethyl acetate and absolute alcohol, m.p. 226°. (Found: C, 55.63; H, 8.64; N, 7.56. $C_{17}H_{32}O_2N_2Cl_2$ requires C, 55.59; H, 8.72; N, 7.63%).

The authors express their sincere thanks to Dr. Mata Prasad, Vice-Chancellor, Vikram University, for providing research facilities and to Dr. B. Pathak of the Department of Applied Chemistry, Calcutta University for his keen interest during the course of the investigation.

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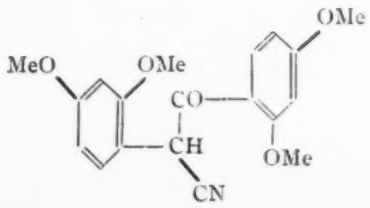
EXPERIMENTS ON THE SYNTHESES OF FURANO COMPOUNDS. PART XVII. SYNTHESIS OF COUMESTROL

By J. N. Chatterjea

Coumestrol has been synthesised by treating the keto-nitrile, obtained by condensing 2:4-dimethoxyphenylacetonitrile with ethyl 2:4-dimethoxybenzoate, with aq. HBr in acetic acid, involving demethylation, hydrolysis and cyclisation.

Bickoff *et al.* (*Science*, 1957, **126**, 969; *J. Amer. Chem. Soc.*, 1958, **80**, 3969, 4381) isolated the plant estrogen, coumestrol, from ladino clover, which, on the basis of degradative studies and synthesis was characterised as 6′:7-dihydroxybenzofuro-(3′:2′-3:4)-coumarin (II), the compound having the same skeletal structure as wedelolactone (Govindachari *et al.*, *J. Chem. Soc.*, 1956, 629). The first synthesis of the parent skeleton was effected in this laboratory from *o*-methoxyphenylacetonitrile in two steps (Chatterjea and Roy, this *Journal*, 1957, **34**, 98), and therefore a synthesis of coumestrol along the same lines appeared attractive. For this purpose, 2:4-dimethoxyphenylacetonitrile was condensed with ethyl 2:4-dimethoxybenzoate to the keto-nitrile (I). On boiling with aqueous hydrobromic acid in acetic acid, this indeed furnished coumestrol by demethylation, hydrolysis and cyclisation, as was evident from the very characteristic bluish violet fluorescence of the reaction mixture in different solvents, but the isolation of the estrogen in substance failed on account of its poor crystallising habit (cf. Bickoff *et al.*, *loc. cit.*) and also due to presence of other obvious byproducts including tar. Possibly purification by Craig's counter-current method, as employed by Bickoff *et al.*, would be useful. Other products isolated are 2-(2′:4′-dihydroxyphenyl)-6-hydroxycoumarone (III: R=H) and α-(2:4-dihydroxyphenyl)-2:4-dihydroxyacetophenone and resorcinol (!), all isolated as their methyl ethers. The coumarone (III: R=Me) has been isolated as a degradation product of coumestrol.



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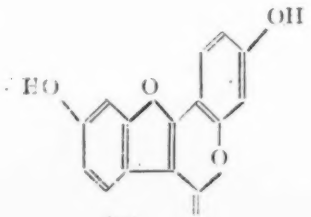

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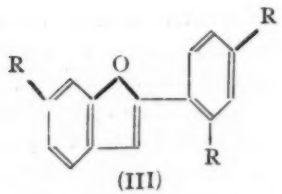

(III)

2 : 4-Dimethoxyphenylacetonitrile required in this investigation was prepared according to Mitter and Moitra (this *Journal*, 1936, **13**, 236) by the usual azlactone synthesis excepting that 2 : 4-dimethoxyphenylpyruvic acid was prepared by the hydrolysis of the related azlactone as the insoluble barium salt, and thus, simplifying the separation from benzoic acid.

EXPERIMENTAL*

2 : 4-Dimethoxyphenylacetonitrile.—The azlactone (10.0 g.) derived from 2 : 4-dimethoxybenzaldehyde (Mitter and Moitra, *loc. cit.*) was boiled under reflux with a mixture of hydrated baryta (20 g.), water (100 c.c.) and alcohol (10 c.c.) for 16 hours, when the evolution of ammonia was practically over. The insoluble *barium salt* of the pyruvic acid was collected and washed thoroughly with water. This was suspended in water, acidified with dilute hydrochloric acid and the precipitated keto-acid (6.5 g.) was converted into 2 : 4-dimethoxyphenylacetonitrile, m.p. 76° (lit.).

Keto-nitrile (I).—A mixture of the above nitrile (6 g.) and ethyl 2 : 4-dimethoxybenzoate (7.0 g.) was added to a suspension of dry sodium methoxide (from sodium, 0.8 g.) in benzene (50 c.c.) and the mixture refluxed for 16 hours. Water (40 c.c.) was added to the cooled mixture and the neutral matter extracted with ether. The alkaline layer was acidified with acetic acid, the whole extracted with ether and washed with sodium hydrogen carbonate. The sticky *keto-nitrile*, obtained on removal of ether, crystallised in course of a few days in presence of alcohol. The compound (5 g.) was obtained in hard prisms from alcohol, m.p. 100°, exhibiting no coloration with ferric chloride. It developed a mustard-yellow colour with H_2SO_4. (Found: C, 67.2 ; H, 5.6. $C_{19}H_{19}O_5N$ requires C, 66.9 ; H, 5.6%).

2-(2′ : 4′-Dimethoxyphenyl)-6-methoxycoumarone.—A mixture of the foregoing keto-nitrile (5 g.), hydrobromic acid (20 c.c., 48%) and acetic acid (20 c.c.) was refluxed for 6 hours and the dark mixture was poured into ice when a black sticky tarry mass was obtained. This was extracted exhaustively with ether. The ethereal solution, which exhibited a brilliant bluish violet fluorescence, was washed with sodium hydrogen carbonate solution and dried ($MgSO_4$). As all attempts to crystallise the resulting gum failed, the whole mass was methylated at the room temperature with methyl sulphate (30 c.c.) in alkaline solution for a period of 3 hours. The methylated product was taken up in ether, dried and distilled in high vacuum. After a forerun of resorcinol dimethyl ether (0.2 g.), the distillate (1.5 g.) was obtained as a glass. This was dissolved in alcohol (6 c.c.) and left in the refrigerator. Colorless crystals

* All m.p.s are uncorrected.

(35 mg.), m.p. 126-28°, of a ketonic product was first deposited. This is probably the hitherto-undescribed α-(2 : 4-dimethoxyphenyl)-2 : 4-dimethoxyacetophenone. (Found : C, 68.3 ; H, 6.3. $C_{18}H_{20}O_5$ requires C, 68.3 ; H, 6.3%). The oxime, obtained as a gum, failed to solidify. The alcoholic mother-liquor slowly deposited a hard crystalline mass (0.35 g.), exhibiting a brilliant bluish fluorescence in the ultraviolet light. The crude compound, m.p. 75-82°, on recrystallisation from aqueous alcohol, was obtained in colorless needles, m.p. 81-82° and identified as the coumarone (III : R=Me); Bickoff *et al.* record m.p. 82° for the compound. (Found : C, 72.0 ; H, 5.7. Calc. for $C_{17}H_{16}O_4$: C, 71.8 ; H, 5 6%).

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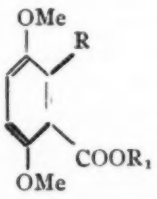
2 : 5-DIMETHOXY-6-NITROBENZOIC ACID (6-NITROGENTISIC ACID DIMETHYL ETHER)

By Pratul Kumar Banerjee and D. N. Chaudhury

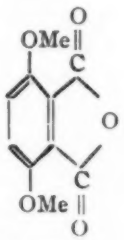
Preparative method for 2 : 5-dimethoxy-6-nitrobenzoic acid (I : R = NO_2 ; R_1 = H) is described and its orientation has been established.

In connection with some projected synthetic sequences, 2 : 5-dimethoxy-6-nitrobenzoic acid was required in quantities, and a search in the literature revealed that Rubenstien (*J. Chem. Soc.*, 1925, 2000) first obtained the acid in unspecified yield by permanganate oxidation of 2 : 5-dimethoxy-6-nitrobenzaldehyde, which he prepared in admixture with its 3-nitro isomer in the ratio of 4 : 1, by the nitration of 2 : 5-dimethoxy-6-benzaldehyde. He ascertained the position of the nitro group in 2 : 5-dimethoxy-nitrobenzaldehyde by the indigotin colour reaction only.

The difficult accessibility of 2 : 5-dimethoxybenzaldehyde (*loc. cit.*), the tedious method of separation of 2 : 5-dimethoxy-6-nitrobenzaldehyde from its 3-nitro isomer by repeated fractional crystallisations and the uncertainty of the orientation, since the presence of the 6-nitro-aldehyde in its other isomers even in traces would also give rise to the same colour test, necessitated us to evolve a preparative method for 2 : 5-dimethoxy-6-nitrobenzoic acid. For this purpose, the starting material of our choice was the readily accessible 2 : 5-dimethoxybenzoic acid (I : R = R_1 = H) (Villani and Lang, *J. Amer. Chem. Soc.*, 1950, **72**, 2301). On direct nitration at 0-2°, it gave almost exclusively 2 : 5-dimethoxy-6-nitrobenzoic acid (I : R = NO_2 ; R_1 = H) in an excellent yield (78%), the orientation of which was established as follows.



(I)



(II)

The nitro-acid (I : R = NO_2 ; R_1 = H) was reduced with sodium dithionite to 6-amino-2 : 5-dimethoxybenzoic acid (I : R = NH_2 ; R_1 = H), the amino group after diazotisation was converted into the nitrile, the crude cyano-acid hydrolysed and directly transformed to the previously known 3 : 6-dimethoxyphthalic anhydride (II) (Graves and Adams, *J. Amer. Chem. Soc.*, 1923, **45**, 2446).

The position of the nitro group was further substantiated by the fact that 2 : 5-dimethoxy-6-nitrobenzoic acid with diazomethane afforded its methyl ester (I : R = NO_2 ;

R_1 = Me), m.p. 122°, which Klemenc (*Monatsh.*, 1914, **35**, 102 ; m.p. 117-18°) had earlier obtained by the action of diazomethane on 2-hydroxy-5-methoxy-6-nitrobenzoic acid.

It is of interest that during the characterisation of the amino-acid (I : R = NH_2 ; R_1 = H), the interaction of its sodium salt with *p*-nitrobenzyl bromide did not proceed in the usual way. The amino group also reacted to yield *p*-nitrobenzyl 2 : 5-dimethoxy-6-*p*-nitrobenzylaminobenzoate (I : R = $NH.CH_2.C_6H_4.NO_2$-*p* ; R_1 = $CH_2\,C_6H_4.NO_2$-*p*) and, as expected, this derived ester did not dissolve in dilute hydrochloric acid nor did it respond to the azo-β-naphthol dye test.

EXPERIMENTAL*

2 : 5-Dimethoxybenzoic Acid (I : R = R_1 = H).—The procedure adopted was essentially the same as that of Villani and Lang (*loc. cit.*), but when the oxidation of 2 : 5-dimethoxyacetophenone was carried out by NaOCl solution, prepared according to their method, the reaction mixture became reddish brown after the addition of only half the specified quantity of the ketone and only a small amount (3-4 g.) of the acid, mostly contaminated with unchanged ketone, could be isolated by us. Oxidation of the ketone (19 g.) was found to proceed without difficulty with (*N*) NaOCl solution, prepared by absorption of Cl_2 (71 g.) in a solution of NaOH (100 g.) in water (500 c.c.) and crushed ice (400 g.), yielding 7 g. of the acid. On concentration of the mother-liquor it gave a further amount (3 g.) of the acid.

2 : 5-Dimethoxy-6-nitrobenzoic Acid (I : R = NO_2 ; R_1 = H).—Finely powdered 2 : 5-dimethoxybenzoic acid (5 g.) was added in portions with stirring during ½ hour to HNO_3 (*d* 1.42, 20 c.c.) at 0.2°. After addition, stirring was continued for 3 hours at 0-2° and the mixture poured in ice-water (250 c.c.) ; the pale yellow precipitate was filtered off, washed with cold water and dissolved in boiling water (*ca.* 300 c.c). On keeping overnight, yellow crystals of 2 : 5-dimethoxy-6-nitrobenzoic acid separated, m.p. 186-87°, yield 4.8 g. On crystallisation from ethyl acetate-petroleum ether (60-80°), followed by recrystallisations from boiling water, the pure product was obtained in yellow prismatic needles (4.5 g), m.p. 194° (Rubenstien, *loc. cit.*, records m.p. 190-92°). (Found : C, 47.3 ; H, 5.2. Calc. for $C_9H_9O_6N$: C, 47.5 ; H, 4.0%).

The nitro-acid (0.5 g.) was treated with an excess of ethereal diazomethane, stirred for half hour and refluxed on a water-bath for 15 minutes. After cooling, the pale yellow solid on crystallisation from methanol (ice-chest) yielded the methyl 2 : 5-dimethoxy-6-nitrobenzoate (0.45 g.) in yellow irregular prisms, m.p. 122° (Klemenc, *loc. cit.*, records m.p. 117-18°) (Found : C, 49.5; H, 4.3. Calc. for $C_{10}H_{11}O_6N$: C, 49.8; H, 4.5%).

6-Amino-2 : 5-dimethoxybenzoic Acid (I : R = NH_2 ; R_1 = H).—Sodium dithionite (8 g.) was added portionwise with stirring to the nitro acid (2.3 g.) in a solution of KOH (2 g.) in water (20 c.c.) at <40° (water cooling). After half an hour at room temperature, the solution was made acid (Congo red) with HCl (conc.) and heated on a

* All m.p.s uncorrected. Micro-analysis by Dr. Gore, Dept. of Chemical Technology, Bombay University.

water-bath for 1 hour while coal gas was bubbled through the solution to remove SO_2. The pale yellow precipitate was collected after cooling, dissolved in a little warm methanol, filtered from sulphur and the filtrate treated with excess water to turbidity and left in the refrigerator. The yellowish crystalline solid that deposited on recrystallisations from benzene-petroleum ether (60-80°) furnished *6-amino-2 : 5-dimethoxybenzoic acid*, m p. 97°, in colorless elongated needles, yield 1.5 g. (Found : C, 55.6 ; H, 6.4. $C_9H_{11}O_4N$ requires C, 54.8 ; H, 5.6%).

A solution of the amino-acid (0.8 g.) in aqueous-alcohol was titrated with alcoholic NaOH (*N*) and after adding a trace of dilute HCl to neutralise the excess alkali (phenolphthalein), the sodium salt was isolated by evaporation to dryness. It was taken up in water (5 c.c.), mixed with *p*-nitrobenzyl bromide (0.75 g.) in alcohol (3 c.c.) and refluxed for 1½ hours. After dilution with water, when kept in the ice-chest overnight, pale yellow crystals of *p-nitrobenzyl 2 : 5-dimethoxy-6-p-nitrobenzylaminobenzoate* (I : R= $NH.CH_2.C_6H_4.NO_2$-*p* ; $R_1 = CH_2.C_6H_4.NO_2$-*p*) separated, which on recrystallisations from ethyl acetate-petroleum ether (60 80°) yielded the pure specimen as yellow prisms, m.p. 186°. (Found : C, 59.6 ; H, 4.6. $C_{23}H_{21}O_8N_3$ requires C, 59.1 ; H, 4.4%). (Calc. for the *p*-nitrobenzyl 2 : 5-dimethoxy-6-aminobenzoate, $C_{16}H_{16}O_6N_2$: C, 57.8 ; H, 4.8%). It is insoluble in hot dilute HCl ; azo-β-naphthol test negative.

3 : 6-Dimethoxyphthalic Anhydride (II).—A suspension of 6-amino-2 : 5-dimethoxybenzoic acid (1.7 g) in HCl (*d* 1.16, 2 c c.) and water (7.3 c.c) was diazotised at 0-5° with $NaNO_2$ (0.76 g.) in water (3 c.c.). After addition of a little urea the filtered solution was poured into a hot solution of KCN (2.4 g.) and $CuSO_4$, $5H_2O$ (2 g.) in water (30 c.c.) and heated on a water-bath for 1½ hours, cooled, acidified (Congo red) with HCl (conc). The precipitated crude cyano-acid was collected and refluxed with aq.KOH (75 c.c., 10%) for 10 hours. The filtered solution was then evaporated to a small bulk, cooled, acidified (Congo red) with HCl (conc.) when the solid (P) separating was filtered off. The filtrate was evaporated to dryness under reduced pressure to a yellow residue (Q). The residues (P) and (Q) were separately extracted with boiling ethyl acetate (3 × 50 c.c. each) and the combined extract reduced to a small bulk, filtered hot from a little dark amorphous impurities and on cooling in the refrigerator 3 : 6-dimethoxyphthalic anhydride separated out in pale yellow prisms, m.p. 258°, sintering at 250°. From the mother-liquor further quantities of the anhydride were collected. Vacuum sublimation (0.8 mm/bath temp. 175-80°), followed by one recrystallisation from ethyl acetate, yielded the pure specimen in yellow rectangular prisms (120 mg.), m.p. 261-62° (Graves and Adams, *loc. cit.*, record m.p. 259-61°). (Found : C, 57.6 ; H, 4.4. Calc. for $C_{10}H_8O_5$: C, 57.7 ; H, 3.8%).

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SEARCH FOR NEW ANTIMALARIALS. PART II. SYNTHESIS OF SOME NEW 1:2-DIHYDRO-1:3:5-TRIAZINES

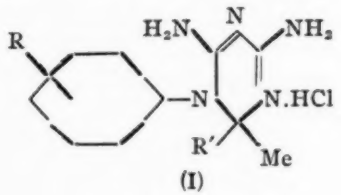
By A. B. Sen and P. R. Singh

Twentyfive 1:2-dihydro-1:3:5-triazines have been synthesised as possible antimalarials; their structural analogy to the active metabolite of chloroguanide has been supported by means of the ultraviolet absorption studies.

A systematic study of the antimalarial action of the dihydrotriazines has revealed that their activity depends on the position, nature and number of the substituents in the dihydrotriazine molecule (Singh *et al.*, *Ind. J. Malar.*, 1954, **8**, 2; Misra *et al.*, *J. Sci. Ind. Res.*, 1955, **14C**, 175).

In continuation of our work on this subject, we have now prepared twentyfive new 1:2-dihydro-1:3:5-triazine derivatives in the form of their hydrochlorides by the condensation of diacetone alcohol or mesityl oxide with cyanoguanidine and different substituted aniline hydrochlorides, with the object of studying the effect of hydroxy and unsaturated groupings on the antimalarial activity. The screening of these compounds for antimalarial activity is in progress at the Malaria Institute of India, Delhi.

The compounds prepared do not form a coloured complex with cuprammonium sulphate and the ultraviolet absorption spectra of some compounds (Table I, No. 1, 3, 7, 10, 12, 13, 17, 18, 21 and 25) with 0.00008% aqueous solution show a common maxima at 241 mμ, characteristic for the 1:2-dihydro-1:3:5-triazines (I) (Modest, *J. Org. Chem.*, 1956, **21**, 4). These studies thus confirm that the dihydrotriazines, prepared, have structure (I), similar to that of the active metabolite of proguanil.



(I)

Experimental

Diacetone alcohol was obtained in 87% yield by the method described by Kyriakides (*J. Amer. Chem. Soc.*, 1914, **36**, 530). Mesityl oxide was prepared according to the method of Hibbert (*ibid.*, 1915, **37**, 1755; "Organic Syntheses", Coll. Vol., 1932, **1**, p. 338).

1:2-*Dihydro*-1:3:5-*triazines*.—A mixture of the substituted aniline hydrochloride (0.1 *M*), dicyandiamide (0.15 *M*) and diacetone alcohol or mesityl oxide (0.2*M*) in 95% ethyl alcohol (50 c.c.) was refluxed on a water-bath with occasional shaking for 15 and

hours respectively. The reaction mixture usually became brownish black or dark brown, and crystals began to separate after $1\frac{1}{2}-8$ hours' refluxing. After completion of the reaction, the reaction products were cooled and crystalline dihydrotriazine derivatives filtered on a Buchner funnel and washed with ethanol. Recrystallisation from ethyl alcohol gave shining crystals.

p-Anisidine, *p*-phenetidine, *p*-chloro-, *p*-bromo-, *p*-iodo-, 3-chloro-4-bromo-, 3 : 5-dibromo-4-hydroxy-, *p*-nitro- and 2:4-dimethyl-aniline, and *p*-toluidine hydrochlorides were condensed both with diacetone alcohol and mesityl oxide ; 2 :4-dichloro-, 3-chloro-4-iodo-, 2-methyl-4-iodo-, *p*-hydroxy- and *o*-ethyl-aniline hydrochlorides were condensed only with diacetone alcohol. The analytical results and m.p. etc. of the 25 dihydrotriazines, thus obtained, are recorded in Table I.

TABLE I

No.	Substitution.	1 :3 :5-Triazines (I). M.P.	Yield.	% Nitrogen. Found.	Calc.	Picrates. M.P.	Formula.	% Nitrogen. Found.	Calc.
				$R' = Me_2C(OH).CH_2$.					
1.	*p*-OMe	220°	66%	20.38	20.50	187-88°	$C_{21}H_{26}O_9N_8$	20.89	20.98
2.	*p*-OEt	205-206°	85	19.61	19.69	190-91°	$C_{22}H_{28}O_9N_8$	20.36	20.42
3.	*p*-Cl	250°	83	20.22	20.23	199°	$C_{20}H_{23}O_8N_8Cl$	20.75	20.80
4.	*p*-Br	215°	88	17.79	17 93	206°	$C_{20}H_{23}O_8N_8Br$	19.11	19.21
5.	*p*-I	248°	89	15.83	15.90	190°	$C_{20}H_{23}O_8N_8I$	17.70	17.78
6.	2:4-Di-Cl	226°	81	18.28	18.40	208-209°	$C_{20}H_{22}O_8N_8Cl_2$	19.40	19 55
7.	3-Cl-4-Br	203-204°	79	16.45	16.47	167°	$C_{20}H_{22}O_8N_8ClBr$	17.99	18.14
8.	3-Cl-4-I	205°	63	14.73	14.83	161°	$C_{20}H_{22}O_8N_8ClI$	16.88	16.85
9.	2-Me-4-I	230-31°	76	15.52	15.50	190-91°	$C_{21}H_{25}O_8N_8I$	17.32	17.39
10.	3 :5-Di-Br-4-OH	242°	91	14.36	14.42	189°	$C_{20}H_{22}O_9N_8Br_2$	16 47	16.52
11.	*p*-OH	209-210°	85	21.34	21.38	203-204°	$C_{20}H_{24}O_9N_8$	21.54	21.54
12.	*p*-NO_2	259-260°	74	23.51	23.57	163°	$C_{20}H_{23}O_{10}N_9$	22.88	22.95
13.	*p*-Me	234°	81	21.43	21.51	187°	$C_{21}H_{26}O_8N_8$	21.59	21.62
14.	2:4-Di-Me	244°	62	20.65	20.62	198°	$C_{22}H_{28}O_8N_8$	20.89	21.06
15.	*o*-Et	206-207°	87	20.56	20.62	190°	$C_{22}H_{28}O_8N_8$	21.00	21.06
				$R' = Me_2C{=}CH$.					
16.	*p*-OMe	221°	84	21.55	21.64	197°	$C_{21}H_{24}O_8N_8$	21.63	21.71
17.	*p*-OEt	215°	85	20.69	20.74	188°	$C_{22}H_{26}O_8N_8$	21.12	21.13
18.	*p*-Cl	238-39°	89	21.30	21.34	197°	$C_{20}H_{21}O_7N_8Cl$	21.39	21.52
19.	*p*-Br	210°	78	18.72	18.79	199°	$C_{20}H_{21}O_7N_8Br$	19.77	19.82
20.	*p*-I	240-41°	88	16.65	16.69	181-82°	$C_{20}H_{21}O_7N_8I$	18.25	18.30
21.	3-Cl-4-Br	209-211°	90	17.23	17.20	187-88°	$C_{20}H_{20}O_7N_8ClBr$	18.65	18.68
22.	3 :5-Di-Br-4-OH	237°	93	14.88	14.98	185°	$C_{20}H_{20}O_8N_8Br_2$	16.89	16.99
23.	*p*-NO_2	269°	84	24.78	24.82	234°	$C_{20}H_{21}O_9N_9$	23.71	23.73
24.	*p*-Me	231°	82	17.96	18.09	184°	$C_{21}H_{24}O_7N_8$	21.88	21.87
25.	2:4-Di-Me	242°	87	21.69	21.77	192°	$C_{22}H_{26}O_7N_8$	21.71	21.79

The *picrates* of the dihydrotriazines were precipitated immediately on mixing the hot saturated aqueous solutions of the dihydrotriazines and picric acid. Recrystallisation from alcohol gave shining yellow crystals (Table I).

The *nitrites* were prepared by a adding solution of sodium nitrite (0.0075*M*) in water (2.5 c.c.) to a solution of the dihydrotriazine hydrochloride (0.0075*M*) in water (50.0 c.c.). Immediately after addition, small crystals of the dihydrotriazine nitrite separated out of the solution. The product was filtered and washed with water. Recrystallisation from hot water gave shining white crystals.

The *bicarbonates* were obtained by adding saturated aqeuous solution of the dihydrotriazine hydrochloride (2.5 c.c.) to a saturated aqueous solution of sodium bicarbonate (5.0 c.c.) and keeping the mixture in a refrigerator overnight. White crystals of the dihydrotriazine bicarbonate, thus formed, were filtered and washed with water.

The nitrites and bicarbonates of the ten dihydrotriazines (Table I: compounds No. 1, 3, 4, 7, 14, 16, 18, 19, 21 and 25) have been prepared and listed in Table II.

TABLE II

	Nitrites.				Bicarbonates.				
Nitrites & Bicarbonates of*	Formula.	M.P.	% Nitrogen. Found.	Calc.	Formula.	M.P.	% Carbon. Found.	Calc.	% Hydrogen. Found.	Calc.
1.	$C_{15}H_{24}O_4N_6$	171°	23.79	23.87	$C_{16}H_{25}O_5N_5$	179°	52.26	52.31	6.77	6.81
3.	$C_{14}H_{21}O_3N_6Cl$	177°	23.55	23.56	$C_{15}H_{22}O_4N_5Cl$	154°	48.50	48.46	5.90	5.92
4.	$C_{14}H_{21}O_3N_6Br$	162°	20.88	20.95	$C_{15}H_{22}O_4N_5Br$	109°	43.25	43.27	5.27	5.29
7.	$C_{14}H_{20}O_3N_6ClBr$	139°	19.27	19.29	$C_{15}H_{21}O_4N_5ClBr$	133°	39.89	39.96	4.65	4.66
14.	$C_{16}H_{26}O_3N_6$	163°	23.87	24.00	$C_{17}H_{27}O_4N_5$	117°	55.96	55.89	7.45	7.40
16.	$C_{15}H_{22}O_3N_6$	178°	25.03	25.15	$C_{16}H_{23}O_4N_5$	164°	54.96	55.01	6.62	6.59
18.	$C_{14}H_{19}O_2N_6Cl$	154°	24.84	24.82	$C_{15}H_{20}O_3N_5Cl$	128°	50.90	50.92	5.61	5.66
19.	$C_{14}H_{19}O_2N_6Br$	152°	21.58	21.68	$C_{15}H_{20}O_3N_5Br$	121°	45.08	45.23	4.99	5.03
21.	$C_{14}H_{18}O_2N_6ClBr$	159°	20.11	20.13	$C_{15}H_{19}O_3N_5ClBr$	127°	41.66	41.62	4.42	4.39
25.	$C_{16}H_{24}O_2N_6$	153°	25.37	25.31	$C_{17}H_{25}O_3N_5$	171°	58.76	58.79	7.23	7.21

* Numbers refer to the dihydrotriazines enlisted in Table I.

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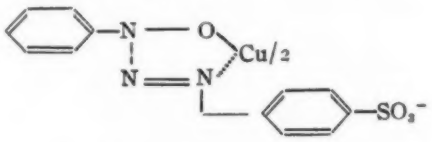
SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES OF METAL COMPLEXES OF 3-HYDROXY-1-*p*-SULPHONATOPHENYL-3-PHENYL-TRIAZINE. PART III. COPPER COMPLEX

By Umesh Chendra Durgapal and N. C. Sogani

Copper forms a pale yellow, water-soluble complex with 3-hydroxy-1-*p*-sulphonatophenyl-3-phenyl-triazine, with an absorption peak at 405 mμ. The *p*H range of constant maximum absorbance is between 4.4 and 6.2. The formula of the complex established spectrophotometrically and conductometrically is determined as CuR_2 (R=reagent). The molecular extinction coefficient is 2.5×10^3 at 425 mμ. The dissociation constant at 25° is 18.28×10^{-10} and the free energy of the complex is -11.92 K cal./mole.

3-Hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine furnishes a pale yellow, water-soluble complex with copper. The complex formation is almost instantaneous and the colour intensity remains unaltered even after 24 hours. It is stable to wide temperature variations. It has an absorption peak at 405 mμ where the excess of the reagent interferes. Hence, this reagent does not offer any good method for the colorimetric estimation of copper. However, the complex can be studied at 425 mμ where the absorbance by the reagent is negligible.

In Parts I and II of the series (this *Journal*, 1958, **35**, 542, 859) the formulae of palladium and molybdenum complexes were established. In the present investigation the formula of copper complex, using spectrophotometric and conductometric methods, has been established. The empirical formula of the complex is CuR_2. The chelate structure may be represented as:



Experimental

Standard copper sulphate (Analar, B.D.H.) solution was prepared and was further diluted to provide $M\times10^{-3}$ copper solution. Reagent solution, buffer solution, instruments etc. were the same as described in Part I (*loc. cit.*).

Spectral Characteristics of Copper Complex.—$M\times10^{-3}$ copper solution (1 c.c.) and $M\times10^{-3}$ reagent solution (15 c.c.) were taken in a 50 c.c. flask and 10% sodium acetate solution (2 c.c.) was added so that after making up to the mark, the *p*H was at about 5.0. Absorbance was measured at different wave-lengths from 380 to 800 mμ, using the reagent solution as blank. The complex showed maximum absorption at 405 mμ. Because of the considerable interference of the reagent at this wave-length, the formula of the complex was studied at 425 mμ where the absorbance by the reagent was almost nil and water was used as a blank solution.

Effect of pH.—Solutions containing the same concentrations of copper and reagent were prepared at different pH values and their absorbance was measured at 425mμ. The range of constant maximum absorbance is from pH 4.4 to 6.2.

Rate of Reaction and Stability of the Complex.—The colour formation of copper complex with the reagent was almost instantaneous and it was very stable. There was no difference in absorbance taken after 4 minutes and after 24 hours.

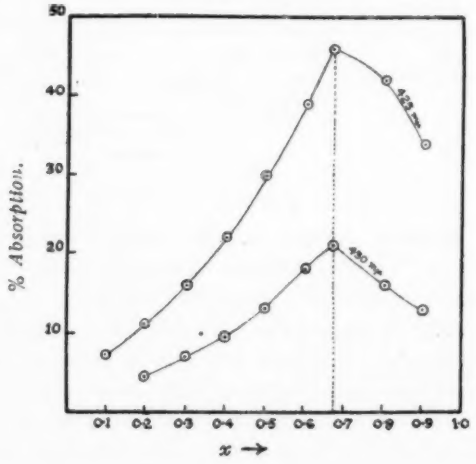
Effect of Temperature on the Reaction.—Samples were heated on a water-bath to 85°, cooled to room temperature and absorbance was measured after making up the volume. There was no difference in the absorbance of this sample and that prepared at room temperature. The complex is thus stable over a wide range of temperature variations.

Nature of the Complex formed.—In a set of experiments, mixtures containing varying proportions of copper : reagent were prepared and the optical densities at different wave-lengths in each case measured. In all the cases the maximum absorption occurred at 405 mμ, thus indicating the formation of only one complex with the reagent (Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437).

Composition of the Complex.—The molar composition of the copper complex was investigated by the following methods.

Job's Method of Continued Variation.—The copper content in the final solution was varied between $2 \times 10^{-5}M$ and $18 \times 10^{-5}M$, and the final pH was kept at about 5.0. Absorbance was measured at 425 and 430 mμ. Fig. 1 shows the curves obtained by applying this method. The maxima at 0.67 indicate the ratio of copper to reagent as 1 : 2.

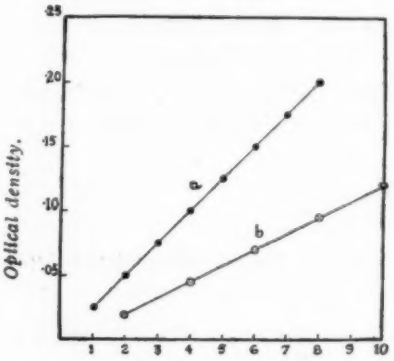
FIG. 1



Slope Ratio Method.—The concentration of the variable component was varied from 1×10^{-5} M to $10 \times 10^{-5}M$ in presence of the excess concentration of 8×10^{-4} M of the constant component. The pH of the solution was kept at about 5.2. Fig. 2 shows

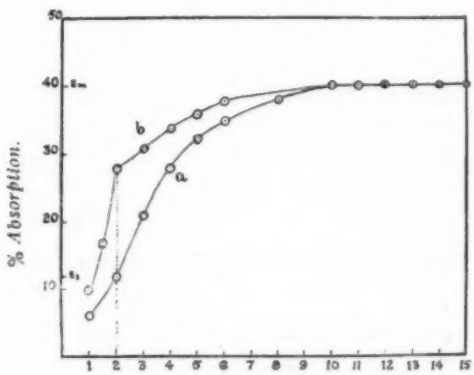
the measured optical density at 425 mμ plotted against the concentration of the variable component. The slopes of the two straight lines give copper : reagent ratio as 1:2.

FIG. 2



Conc. of variable component ($M \times 10^5$)
a refers to Cu varying.
b ,, reagent ,,
Conc. of const. component = $8 \times 10^{-4}M$.
*p*H = 5.2. λ = 425 mμ.

FIG. 3.

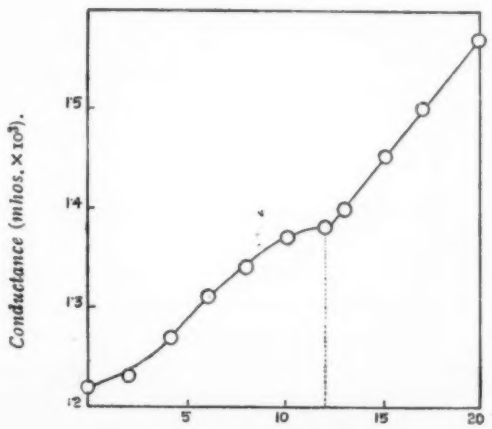


Reagent: Cu (*M*/*M*)
Conc. of Cu = $2 \times 10^{-5}M$.
*p*H = 5.7-5.8.
λ = 425 mμ.

Molar Ratio Method.—A series of solutions was prepared at about *p*H 5.8 with a constant concentration of copper at $2 \times 10^{-5}M$ and keeping the copper to reagent ratio at 1:1 to 1:15. Fig. 3 (curve *a*) gives the molar ratio of copper to reagent for constant maximum absorption as 1:10. By adding 1 c.c. of 1 *M*-KCl solution to suppress the dissociation of the complex, a break is obtained (Fig. 3, curve *b*) at a ratio of 2 moles of the reagent to 1 mole of copper.

Conductivity Method.—The method was the same as described in Part I. Fig. 4 shows the conductivity values plotted against c. c. of the reagent added. The break in the curve at 12 c.c. of the reagent solution indicates CuR_2 as the formula of the complex. This is in agreement with the spectrophotometric results.

FIG. 4



Reagent added ($M \times 10^{-3}$) *in c.c.*

Discussion

The dissociation of the complex may be written as:

CuR_2	$\rightleftharpoons$	Cu^{2+}	$+ 2R^-$	
C		0	0	Initial conc.
$C(1-\alpha)$		αC	$2\alpha C$	Final conc.

where C is the total concentration of the complex in moles per litre, assuming no dissociation, and α is the degree of dissociation. The dissociation constant K is given by the equation

$$K = \frac{\alpha C \times (2\alpha C)^2}{C(1-\alpha)} = \frac{4\alpha^3 C^2}{1-\alpha}.$$

The value of α may be obtained from the curve 'a', in Fig. 3 by the following relationship:

$$\alpha = (E_m - E_s)/E_m = (40-12)/40 = 0.7,$$

where the terms have their usual significance. The concentration C of the complex is equal to the total concentration of copper, which is $2 \times 10^{-5} M$.

By substituting these values in the above equation, the value of K at 25° comes to 18.28×10^{-10}. Hence, the stability constant K of the complex is equal to 5.46×10^5.

Molecular extinction coefficient ϵ is equal to the slope of the straight line 'a' in Fig. 2.

$$\epsilon = \text{Slope } (a) = 2.5 \times 10^3.$$

The standard free energy of formation of the complex from copper sulphate and 3-hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine is calculated from the relation,

$$\Delta F^\circ = RT \ln K,$$

where the terms have their usual significance. The value of ΔF° works out to be $-11.92\,K$ cal./mole at 25°.

The authors express their gratitude to Principal Bhim Sen for providing facilities n the college.

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CHEMISTRY OF EXTRACTIVES FROM HARDWOOD. PART I. CONSTITUENTS OF THE HEARTWOOD OF *AEGLE MARMELOS* CORREA

By Mrs. A. Chatterjee and S. K. Roy

The heartwood of *Aegle marmelos* Correâ contains several chemical components from which a furoquinoline alkaloid, 'dictamnine', $C_{12}H_9NO_2$, a dihydrofurocoumarin, 'marmesin', $C_{14}H_{14}O_4$, β-sitosterol, and a hitherto-unidentified neutral compound, m.p. 133-34°, have been isolated.

The heartwood extractives of *Aegle marmelos* Correâ (Fam. Rutaceae) have been examined for its chemical components. From the ether extract of the milled plant materials, several compounds have been isolated of which only three have been characterised.

One of the constituents is found to be identical with dictamnine, 4-methoxyfuroquinoline, m.p. 133° (yield 0.0005%), occurrence of which has been reported so far only in two Rutaceous species, viz., *Dictamnus albus* Linn (Thoms, *Ber. deut. Pharm. Ges.*, 1923, **33**, 68) and *Skimmia repens* Nakai (Asahina *et al.*, *Ber.*, 1930, **63**, 2045).

The second component has been characterised as a dihydrofurocoumarin, marmesin, $C_{14}H_{14}O_4$, m.p. 190° (yield 0.0002%). This coumarin derivative was earlier isolated from the mature bark of the same plant by one of the present investigators (Chatterjee and Mitra, *J. Amer. Chem. Soc.*, 1949, **71**, 606). Recently marmesin has been isolated by Egyptian workers from the fruits of *Ammi majus* Linn (Fam. Umbelliferae) (Abu-Mustafa *et al.*, *Nature*, 1958, **182**, 54), reputed for their use in the treatment of leucoderma.

The third neutral component has been shown to be β-sitosterol, $C_{29}H_{50}O$, m. p. 138-39°. Characterisation of the fourth constituent, m.p. 133-34°, is under progress.

Experimental

The dried and milled heartwood of *Aegle marmelos* Correâ (2.0 kg.) was soxhletted with ether for 48 hours. The green ether extract was washed with 2*N*-HCl (200 c.c.) (A) to separate the basic constituents, if any. The ether solution was subsequently washed with water, dried over anhydrous sodium sulphate and concentrated when a crystalline solid, adherent with a gummy mass, separated (3.0 g). It was dissolved in benzene and subjected to chromatographic resolution through Brockmann alumina (32 cm. × 2 cm), using benzene and later ethyl acetate as developers. Eluents were collected in fractions of 15 c.c. each (Table I).

TABLE I

Fractions.	Residue on evaporation of solvent.	Fractions	Residue on evaporation of solvent.
	With benzene as eluent.		With ethyl acetate as eluent.
1-4	Oily mass	21-23	Yellow solid, m.p. 156-62°
5-10	Solid with yellow colour, m.p. 129-31°	24-30	Yollowish solid, m.p. 176-78°
11-17	White solid, m.p. 134-37°	31-32	Nil
18-20	Nil		

Isolation of Marmesin.—Fractions (21-30) were crystallised from a mixture of benzene-petroleum ether (b.p. 40-60°), m.p. 179-82°. The product was found to be a coumarin derivative. It sublimed at 200° under 0.01 mm and crystallised from petroleum ether (b.p. 40-60°), m.p. 190°. (Found in a dry sample: C, 67.96; H, 5.37. Calc. for $C_{14}H_{14}O_4$: C, 68.29; H, 5.69%). Melting point of this compound remained unchanged when admixed with an authentic sample of marmesin.

Isolation of β-Sitosterol.—Fractions (11-17) on crystallisation from a mixture of methanol and ethyl acetate (1 : 1) yielded white flakes, m.p. 138-39° The compound developed a green colour in the Liebermann-Burchard test, $[\alpha]_D^{28} - 31°.12$ (in chloroform). (Found in a dry sample: C, 83.74; H, 12.23. Calc. for $C_{29}H_{50}O$: C, 84.05; H, 12.09%).

Acetyl Derivative of β-Sitosterol.—β-Sitosterol (0.1 g.) was treated with 1.0 c.c. of acetic anhydride and 2 drops of pyridine and the mixture was heated on a water-bath for 6 hours. The reaction mixture was added to crushed ice and kept in the refrigerator overnight. The solid separating was filtered, washed with water and crystallised several times from a mixture of methanol and acetone in colorless flakes, m.p. 125-26°, yield 0.07 g. (Found in a dry sample: C, 81.69; H, 11.52. Calc. for $C_{31}H_{52}O_2$: C, 81.57; H, 11.40%).

Benzoyl derivative of β-sitosterol was similarly prepared from a mixture of β-sitosterol (0.1 g.), benzoyl chloride (1 c.c.) and 2 drops of pyridine. The solid separating was filtered, washed with 2% aqueous KOH (till free from benzoic acid) and then with water and finally crystallised from a mixture of methanol and acetone, m.p. 144-45°, yield 0.05 g. (Found in a dry sample: C, 83 42; 10.61. Calc. for $C_{36}H_{54}O_2$: C, 83.39; H, 10.42%).

β-Sitosterol, its acetyl and benzoyl derivatives did not show any change in melting point when admixed with their authentic samples.

Isolation of unidentified Neutral Compound.—Fractions (5-10) were crystallised from petroleum ether (b.p. 60-80°) in fine colorless needles, m.p. 133-34°. (Found in a dry sample: C, 64.54; H, 9.13; C.Me, 0.0; active H, 0.0%).

Isolation of Dictamnine.—The hydrochloric acid washings (A) were cooled in ice and basified with sodium carbonate (*p*H 7-8) when the aqueous solution became turbid. The base separating was extracted with ether. The extract was washed with water, dried over anhydrous sodium sulphate and concentrated, when a brown oil was obtained (0.3 g.). The product was subjected to chromatographic purification through Brockmann alumina

(10 cm × 2 cm), using petroleum ether (b.p. 60-80°), benzene and later a mixture of benzene and ethyl acetate (1 : 1) as developers. Eluents were collected in fractions of 15 c.c. each (Table II).

TABLE II

Eluents.	Fractions.	Residue after evaporation of solvent.
Petroleum ether (b.p. 60-80°)	1-4	Yellow oil.
Benzene	5-8	Non-crystallisable, brown, gummy residue.
,,	9-10	Nil
Benzene : ethyl acetate (1 : 1)	11-14	Brown solid, m.p. 112-17°
,,	15-16	Nil

Fractions (11-14) were crystallised from a mixture of benzene and ethyl acetate (1 : 1) in stout prismatic crystals, m.p. 133°. (Found in a dry sample : C, 72.29 ; H, 4.64 ; N, 6.98 ; -OMe, 15.38. Calc. for $C_{12}H_9O_2N$: C, 72.36 ; H, 4.52 ; N, 7.03 ; -OMe, 15.57%). The melting point of the alkaloid did not change when admixed with an authentic sample of dictamnine.

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POSSIBLE ANTITUBERCULOUS COMPOUNDS. PART VI. PREPARATION OF PHENYL*cyclo*HEXYLAMIDINES

By Vinay S. Misra and Md. Imtiaz Husain

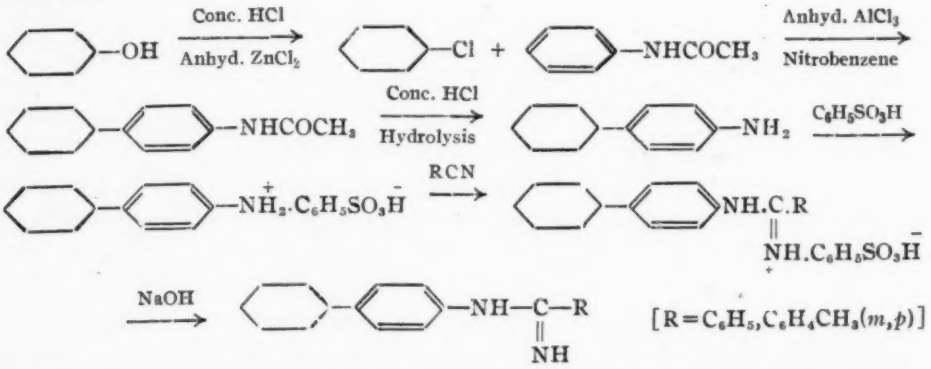
With a view to increasing the lipoid solubility and surface area of *N*-4-diphenylylamidines, compounds of known antitubercular activity, several *N*-4-phenyl*cyclo*hexylamidines have been prepared.

A series of 4′-alkyl-4-*N*-diphenylylamidines, possessing greater antitubercular activity than *N*-4-diphenylylamidines, have been described previously (this *Journal*, 1952, **29**, 695 ; 1953, **30**, 43).

In the present communication, we have tried to increase the surface area of *N*-4-diphenylylamidines by replacing the benzene ring (free of amino group) of 4-aminodiphenyl by a *cyclo*hexyl ring and subsequently preparing three new amidines by the method of Oxley and Short (*J. Chem. Soc.*, 1946, 147).

4-Aminophenyl*cyclo*hexane was prepared by us by the application of the Friedel-Crafts synthesis, so far not tried for this compound, although it was prepared by the nitration of phenyl*cyclo*hexane and the subsequent reduction of the nitro compound (Beilstein, 1922, p. 504 ; 1929, p. 1209).

*cyclo*Hexyl chloride was condensed with acetanilide to yield 4-acetaminophenyl-*cyclo*hexane (vide Experimental), the latter affording 4-aminophenyl*cyclo*hexane, in a poor yield, on hydrolysis ; a considerable amount of tarry product was also produced. The identity of 4-aminophenyl*cyclo*hexane with that mentioned in the literature was confirmed by the nitrogen estimation as well as by melting point determination.



4-Aminophenyl*cyclo*hexane was converted into 4-phenyl*cyclo*hexane ammonium benzenesulphonate by adopting the method of Bauer and Cymerman (*J. Chem. Soc.*, 1950, 1826).

The benzenesulphonate on heating with four different nitriles and adopting the usual method yielded the amidine benzenesulphonates. The latter were obtained in a crystalline form after repeated refluxing with ether. The benzenesulphonates were subsequently converted into amidines by the usual process of basification and and isolation. The amidines were obtained in a crystalline form, except in one case. The antitubercular activity of the amidines will be reported later on.

EXPERIMENTAL

*cyclo*Hexyl chloride was prepared by following the method described by Vogel ("Text Book of Organic Preparation", 1956, p. 275) in pure form in 90% yield, b.p. 141°.

4-*Aminophenyl*cyclo*hexane*.—Acetanilide (15 g., 1 *M*), anhydrous aluminium chloride (22 g., 1.5 *M*) and dry nitrobenzene (50 c c.) were taken in a r.b. flask fitted with a reflux condenser with a calcium chloride guard-tube and a dropping funnel containing *cyclo*hexyl chloride (13 g.). The latter was added dropwise under cooling. After the whole of *cyclo*hexyl chloride had been added and the evolution of HCl gas had ceased, the reaction mixture was warmed on the water-bath at 50° when more HCl gas was evolved ; it ceased after about 1½ hours. Pieces of crushed ice were added with shaking to the reaction mixture, when an oily sticky mass was obtained. The latter was subjected to steam distillation to remove the excess of the solvent. After removal of the nitrobenzene a black tarry mass was left in the flask, which solidified on cooling. The product was hydrolysed with HCl (conc.) for 4 hours, during which not more than 1/8 th part of the mass went into solution. After cooling, the solution was filtered off and basified with aqueous sodium carbonate to get a brown precipitate. The latter was filtered off and dried. The crude product was recrystallised from ligroin to afford a brown powder, yield 3 g. (12% of theory), m.p. 56° (lit. m.p. 56-57°). (Found : N, 7.84. Calc. for $C_{12}H_{17}N$: N, 8%).

4-*Phenyl*cyclo*hexane Ammonium Benzenesulphonate* (A).—4-Aminophenyl*cyclo*hexane (2.5 g., 1 *M*) was stirred in 150 c.c. of dry ether, and benzenesulphonic acid (2.5 g., 1 *M*), dissolved in methanol, was added slowly with shaking. A pinkish white solid separated out which was filtered, dried and recrystallised from hot water as a pink amorphous powder, m.p. > 265°, yield 4.5 g. (90% of theory). (Found : N, 3.36. $C_{18}H_{25}O_4NS$ requires N, 3.9%).

4-*Phenyl*cyclo*hexene*-m-*tolylamidine*.—The above compound (A) (0.5 g.) was mixed with *m*-tolylnitrile (excess, 0.8 c.c.) in a 100 c.c. r.b. flask fitted with a reflux condenser and a gas absorption tower and the mixture heated at 225-30° (external bath temperature) for 4½ hours. The contents were then cooled and triturated with boiling ether when a brown powder was obtained which was recrystallised from hot water to yield a white amorphous substance, m.p. 146-47°, yield 46% of theory (0.35 g.).

The amidine benzenesulphonate (0.3 g.) was suspended in water and an excess of 5-*N*-NaOH solution was added to it and the mixture stirred for 5 hours. The amidine, so obtained, was filtered to afford a white powder, m.p. 121-22°, yield 0.18 g. (66 % of theory). (Found : N, 9.03. $C_{20}H_{24}N_2$ requires N, 9.58%).

4-Phenylcyclohexane-p-tolylamidine was obtained in a similar way by heating (A, 0.5 mg.) with *p*-tolylnitrile (1 g., excess) for 5 hours at 225-30°, and liberating the amidine as a brown amorphous powder, m.p. 168-69,° yield 50% of the theory. (Found : N, 8.98. $C_{20}H_{24}N_2$ requires N, 9.58%).

4-Phenylcyclohexane benzamidine was obtained by heating under reflux for 4½ hours at 225-30°, the compound (A, 0.5 g.) and benzonitrile (0.9 g., excess) as a brown solid, m.p. > 255°, yield 40% of theory. (Found : N, 9.84. $C_{19}H_{22}N_2$ requires N, 10.07%).

The compound (A, 0.5 g.) and *o*-tolylnitrile (1 g., excess) were heated under reflux for 4½ hours at 225-30° and the contents after cooling were triturated with boiling ether when a dark brown solid was obtained, but the amidine could not be isolated on basification with sodium hydroxide.

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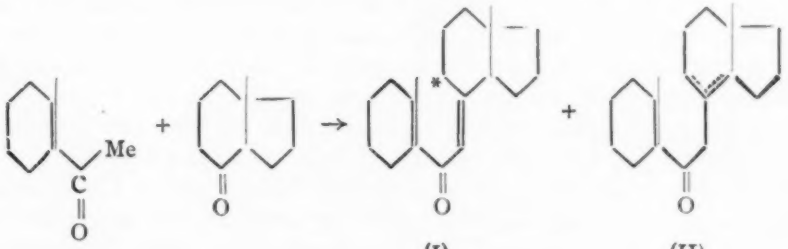
STUDIES IN MICHAEL CONDENSATION. PART IV. CONDENSATION OF 8-METHYL-BI*cyclo*-[4:3:0]-NONANONE-4 WITH 1-METHYL-2-ACETYL*cyclo*HEXENE

By Sisir Kumar Sen Gupta and Bidyut Kamal Bhattacharyya

The condensation of 1 methyl-2-acetyl*cyclo*hexene with 8-methyl bi*cyclo*-[4:3:0]-nonanone-4 in presence of a base furnishes (I) and (II); the presence of two double bonds has been established by hydrogenation to (III). The mixture (I and II), on treatment with $LiAlH_4$ and acid, affords either a mixture of ring-closed products (VIII and IX) or (X), depending on the condition and the acidic reagent. The mixture (VIII and IX) reacts with maleic anhydride to yield an adduct. The cyclised dienes furnish on dehydrogenation Diels' hydrocarbon. The unsaturated ketone (XII) on catalytic hydrogenation affords (XIII), indicating that the β-side is less hindered, and on treatment with $LiAlH_4$, followed by acid, affords a diene (XV) or (XIV).

Banerjee *et al*. (this *Journal*, 1957, **34**, 715) suggested that the product, obtained by Bagchi and Banerjee (*ibid.*, 1946, **23**, 397) by the condensation of 1-methyl-2-acetyl*cyclo*hexene with 8-methyl-bi*cyclo*-[4:3:0]-nonanone-4 in the presence of a base, should be regarded as a mixture. An investigation of the aforementioned product has now been reported.

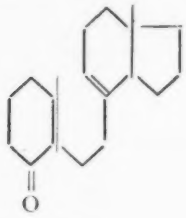
The distilled condensation product, on chromatography on alumina, furnished two fractions: (A), λ_{max} 251 mμ (ϵ 4,800) and (B), λ_{max} 247 mμ (ϵ 4,800); the residual material was chromatographed and distilled to afford another liquid fraction (C) which, though expected to be a tetracyclic compound according to the observation of Braude and Wheeler (*J. Chem. Soc.*, 1955, 329), did neither show any absorption in the ultraviolet region nor provide correct analyses. The ultraviolet absorption spectra of (A) and (B) clearly pointed to the structures (I) and (II), with fraction (B) consisting mainly of the compound (II) while (A) being presumably a mixture of the compounds (I) and (II) (Braude and Wheeler, *loc. cit.*).



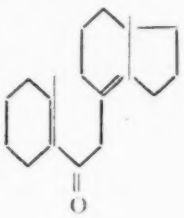
(I) (II)

The predominance of (II) over (I) may be ascribed to electronic (Ingold, "Structure and Machanism in Organic Chemistry", 1st ed., the George Banta Publishing Company, Wisconsin, U.S.A., 1953) and steric factors (Turner, *J. Amer. Chem. Soc.*, 1958, **80**, 1424). Again of the structures, (IIa) and (IIb), the former appears to

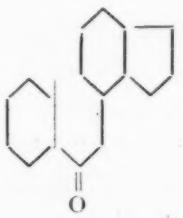
be the favoured one, because abstraction of a proton from the position marked *i (I) is easier compared with that from the ring juncture.



(IIa)



(IIb)



(III)

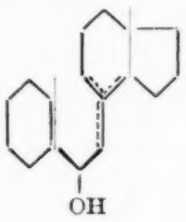
The low intensity of the ultraviolet absorption of (A) and (B) should be ascribed to the hindered *s-trans* configuration (Braude *et al.*, *J. Chem. Soc.*, 1949, 1890; 1950, 2014 ; 1952, 1419).

The aforementioned fractions failed to furnish any solid derivative. The presence of the two double bonds was proved by hydrogenation of (A and (B), separately. It may be mentioned that the rate of hydrogenation of (A) was faster than that of (B) (vide Experimental). The hydrogenated product (III) furnished wo isomeric crystalline 2 : 4-dinitrophenylhydrazones in poor yield (cf. Johnson *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 3726).

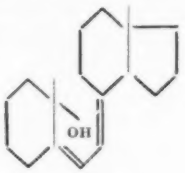
The attempt to prepare a triene from the aforementioned unsaturated ketones resulted, as described below, in products similar to those obtained by Braude and Wheeler (*loc. cit.*) with Huber's compound (*Ber.*, 1938, **71**, 725).

Reduction of the mixture of (I) and (II) with lithium aluminium hydride furnished a product showing absorption in the ultraviolet at 250 mμ (ε 800) and 284 mμ (ε 150). The absorption at the lower wave-length may be due to the traces of the isomeric alcohol (V), formed by the powerful tendency of the alcohol (IV) to undergo rapid anionotropic rearrangement. The structure (V) should be preferred due to the hyperconjugative effect of a methyl group (Braude *et al.*, *J. Chem. Soc.*, 1950, 2007, 2014). It should be mentioned that the reduction product, on repeated distillations, afforded a product showing peaks only at 275 mμ (ε 1,250) and 284 mμ (ε 1,280) ; these peaks may be ascribed to the presence of open-chain trienes (VI) or cyclised homoannular dienes. The question of the formation of cyclised products in preference to open-chain trienes still remains undecided. The aforementioned reduction product on treatment with *p*-toluenesulphonic acid in benzene furnished a product showing absorption at 254 mμ (ε 6,200) and 285 mμ (ε 8,900). This, on hydrogenation over either 10% palladium on charcoal in ethanol or platinum oxide in acetic acid, absorbed only two moles of hydrogen. The hydrogenated product was resistant to the action of perbenzoic acid, thus indicating that cyclisation had taken place with the formation of tetracyclic dienes during the acid treatment of alcohols. The cyclisation might have proceeded (Linstead *et al.*, *ibid.*, 1937, 1136, 1140; 1940, 720; Schinz, *Helv. Chim. Acta*, 1949, **32**, 2556; 1950, **33**, 1129 ; 1952, **35**, 2406 ; Eschenmoser, *ibid.*, 1954, **37**, 964 ; Schinz *et al.*,

ibid., 1957, **40**, 2191; Stork and Burgstahler, *J. Amer. Chem. Soc.*, 1955, **77**, 5c(8) through the carbonium ion (VII) to afford a mixture of dienes (VIII and IX).

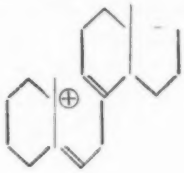


(IV)

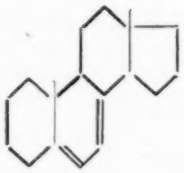


(V)

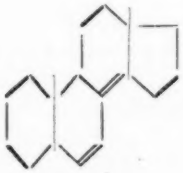
(VI)



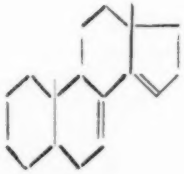
(VII)



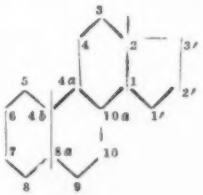
(VIII)



(IX)



(X)



(XI)

The absorption at lower wave-length is ascribed to the diene (IX) from similar absorption of $\Delta^{6:8(14)}$ -steroidal dienes, such as ergosta-6 : 8(14) : 22-trien -3β-ol (Barton and Bruun, *J. Chem. Soc.*, 1951, 2728), while that at the longer wave-length should be ascribed to the diene (VIII) from the similarity in absorption with ergosterol and 7-dehydrocholesterol (Huber *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 609; Beilstein *et al.*, *J. Org. Chem.*, 1949, **14**, 433). This mixture of dienes deteriorates very easily in contact with air, a property manifested by 7-dehydrocholesterol and similar substances.

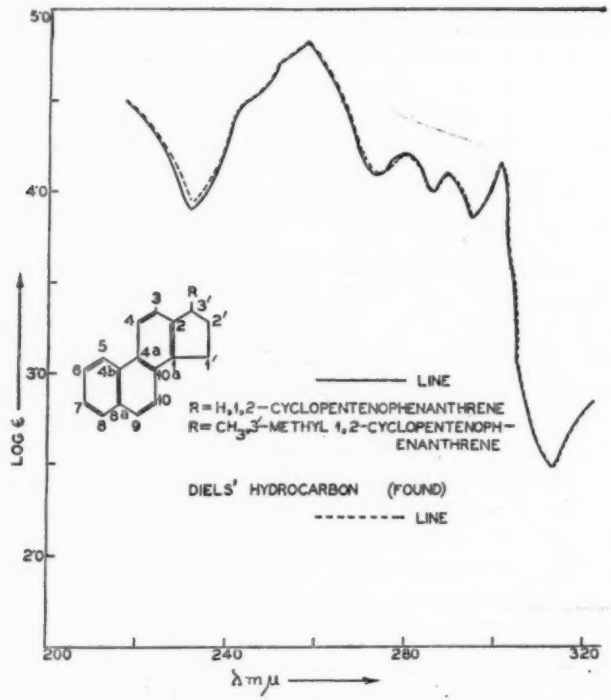
On the other hand, the unsaturated alcohols, when subjected to dehydration under a more drastic condition with fused potassium hydrogen sulphate, afforded another diene (X). The ultraviolet absorption at 245 mμ (ε 8,500) together with the fact that it absorbs on catalytic hydrogenation two moles of hydrogen, clearly points to the structure and the position of the double bonds (Barton and Brooks, *J. Chem. Soc.*, 1951, 257; Woodward and Barton, *ibid.*, 1957, 1139; Feiser, Rosen and Feiser, *J. Amer. Chem. Soc.*, 1952, **74**, 5397). The saturated compound (XI), obtained from (X), had different refractive index from the aforementioned (XI), formed by hydrogenation of the mixture (VIII and IX) and was indifferent to perbenzoic acid. The diene (X) was more stable in air than the mixture of (VIII) and (XI) which, on treatment with fused potassium hydrogen sulphate, rearranged to (X), as indicated by the ultraviolet absorption and refractive index. Furthermore, the diene (X) remained unchanged on treatment with *p*-toluenesulphonic acid.

In order to substantiate the presence of cisoid diene (VIII) in the mixture, it was treated with maleic anhydride and the resulting adduct was converted into the crystalline *N*-phenylmaleimide (Eck and Hellingsworth, *J. Amer. Chem. Soc.*, 1942, **64**, 140;

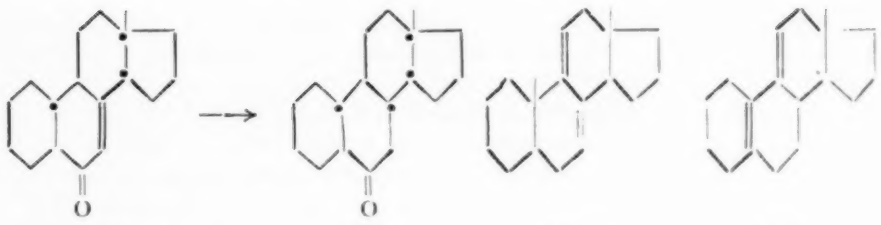
Windaus *et al.*, *Annalen*, 1938, **534**, 22; Inhoffen, *ibid.*, 1938, **508**, 81; Schenk *et al.*, *Ber.*, 1936, **69B**, 2696; Conroy, *J. Amer. Chem. Soc.*, 1952, **74**, 3046; Braude and Wheeler, *loc. cit.*); an increase in concentration of the diene (IX) in the unchanged mixture was clearly indicated by the ultraviolet absorption.

Dehydrogenation of the dienes (VIII, IX and X) over 30% palladium on carbon afforded in poor yield Diels' hydrocarbon "$C_{18}H_{16}$", identified through its *s*-trinitrobenzene complex. The ultraviolet absorption spectrum was found to be completely identical with that of 1:2-*cyclo*pentenophenanthrene and Diels' hydrocarbon. Similar migration of angular methyl group has been observed by various workers (Cook and Hewitt, *J. Chem. Soc.*, 1933, 1019; 1935, 445; Bergmann and Bergmann, *ibid.*, 1939, 1019; Rosenheim and King, *Chem. Ind.*, 1933, 299; Bergmann and Bergmann, *ibid.*, 1936, 272; Kon and Wolman, *J. Chem. Soc.*, 1939, 794; Linstead *et al.*, *ibid.*, 1937, 1146; Johnson *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 3726).

FIG 1



Djerassi *et al.* (*J. Amer. Chem. Soc.*, 1953, **75**, 3496; 1957, **79**, 3835) reduced Δ^8-22a:25a:5α:14β-spirosten-3β-ol-11-one with lithium and ammonia as well as with hydrogen on palladium catalyst and isolated the saturated 8β:9α and 8α:9α compounds respectively.



(XII) (XIII) (XIV) (XV)

With a view to finding out the role of the 4b-methyl group in hydrogenation of perhydro*cyclo*pentanophenanthrene system, the compound (XII) (Banerjee *et al.*, *loc. cit.*) was hydrogenated, and the saturated ketone (XIII) was found to be identical with the product obtained by chemical reduction (Banerjee *et al.*, *loc. cit.*). Of the two isomeric saturated ketones, the one produced by the chemical reduction is expected to be thermodynamically more stable (XIII : 5e, 1a). The production of (XIII) by catalytic hydrogenation suggests that the β-side of the molecule is less hindered due to absence of 4bβ -methyl group and folding of the *cyclo*pentane ring on the α-side of the molecule, in contrast to the behaviour of the aforementioned spirostene with a 4bβ-methyl group.

The compound (XII), on treatment with lithium aluminium hydride followed by *p*-toluenesulphonic acid, afforded an oily diene, λ_{max} 245 mμ (ϵ 13,800). The ultraviolet absorption suggests that it is a heteroannular diene and the structure (XIV) may be assigned to this diene from analogy with the absorption of $\Delta^{7:9(11)}$ -steroidal dienes (Wendler *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 3252 ; Barton and Brooks, *loc. cit.*). It should be pointed out that the other alternative structures, excepting (XV) involving the ring A, could be eliminated from the absorption of C_{19}-norcoprosta-dienes (Ellis and Petrow, *J. Chem. Soc.*, 1952, 2246).

* Experimental

Condensation of 1-Acetyl-2-methylcyclohexene with 8-Methyl-bicyclo-[4:3:0]-nonanone-4.—The condensation was carried out according to the procedure of Banerjee *et al.*, *loc. cit.*) with potassium metal (0.86 g.), butanol^t (21.5 c.c.), 8 methyl-bi*cyclo*-[4:3:0]-nonanone-4 (3 04 g.), 1-methyl-2-acetyl*cyclo*hexene (3.03 g., λ_{max} 245 mμ, ϵ 5,000) and benzene (40 c.c.). During the addition of the solution of ketones to potassium butoxide^t in an atmosphere of nitrogen, the reaction mixture turned orange which changed to rose-red on keeping for 48 hours. After working up, the orange oil was fractionated : (i) 70-80°/3mm (1.2 g.); (ii) 60-65°/0.4 mm (0.9 g.); (iii) 140-60°/0.4 mm (3 g.), a slightly coloured oil, λ_{max} 245 mμ (ϵ 4,500). The third fraction was evaporatively redistilled, b.p. 115-20°/0.2 mm. (Found : C, 84.19 ; H, 9.75. Calc for $C_{19}H_{28}O$: C, 83.82 ; H, 10.29%).

The residue (1 g.) of the aforementioned distillation was dissolved in petroleum ether (60-80°) and chromatographed on alumina (50 g.) to furnish an oil (200 mg.),

* All melting points are uncorrected. The ultraviolet absorption spectrum was examined by the Unicam spectrophometer, S.P. 500 in ethanolic solution.

eluted with the above solvent. It was evaporatively distilled, b.p. 200-10°/0.2 mm. (Found: C, 85.82; H, 9.13%), showing no ultraviolet absorption between 220 and 250 mμ.

A solution of the aforementioned distillate (iii, 2.7 g.) in petroleum ether (60-80°) was chromatographed on alumina (90 g.). The material (0.9 g.), eluted in first few fractions, showed λ_{max} 251 mμ (ε 4,800). The material, eluted in the later fractions, on evaporative distillation, furnished an oil (1.7 g.), b.p. 115-20°/0.2 mm, n_D^{25} 1.5247, λ_{max} 248 mμ (ε 4,800), which failed to furnish any solid semicarbazone or 2:4-dinitrophenylhydrazone. (Found: C, 83.67; H, 9.85. $C_{19}H_{28}O$ requires C, 83.82; H, 10.29%).

Since the separation of the mixture was not sharp, as indicated by ultraviolet absorption, the aforementioned material (0.9 g.) was rechromatographed on alumina (50 g.), using the same solvent. The material, eluted in the first few fractions, was evaporatively distilled to give an oil (A, 250 mg.), b.p. 100-105°/0.1 mm, λ_{max} 251 mμ (ε 4,800), n_D^{25} 1.5250. (Found: C, 83.58; H, 9.86. $C_{19}H_{28}O$ requires C, 83.82; H, 10.29%). The meterial, eluted in the latter fractions, was evaporatively distilled to furnish an oil (B, 650 mg.), b.p. 105-10°/0.1 mm, λ_{max} 247 mμ (ε 4,800), n_D^{25} 1.5246. Both these fractions were found to deteriorate rapidly in air.

1-*Methyl*-2-(8-*methyl*-bicyclo[4:3:0]-*nonyl*-4-*acetyl*)-cyclo*hexane*.—(*a*). A solution of (B, 410 mg.) in methanol (20 c.c.) was hydrogenated over 10% palladium on carbon (100 mg.). The first mole of hydrogen was absorbed in 2 hours, the second mole in another 20 hours. The catalyst was filtered off and the clear filtrate on evaporation of the solvent and evaporative distillation of the residue furnished an oil (400 mg.), b.p. 110-15°/0.2 mm, n_D^{25} 1.4952. (Found: C, 82.61; H, 11.59. $C_{19}H_{32}O$ requires C, 82.61; H, 11.59%).

The crude 2:4-dinitrophenylhydrazone, prepared from the saturated ketone (100 mg.) and 2:4-dinitrophenylhydrazine (60 mg.) in acetone-free methanol (10 c.c.) in presence of three drops of HCl (conc.), was an ill-defined solid (80 mg.), m.p. 80-86°, which on chromatography on alumina, followed by repeated crystallisations from a mixture of equal volumes of ethyl acetate and methanol, furnished two isomeric crystalline 2:4-dinitrophenylhydrazones: (*i*) yellow plates, m.p. 185-86° (decomp.) with shrinkage at 182° (Found: C, 66.47; H, 8.25. $C_{25}H_{36}O_4N_4$ requires C, 65.79; H, 7.89%); (*ii*) yellow needles, m.p. 144-46° (decomp.). (Found: N, 12.58. $C_{25}H_{36}O_4N_4$ requires N, 12.28%). The yellow needles were more soluble than the plates.

(*b*). Similar hydrogenation of the fraction (A, 100 mg.) in methanol (10 c.c.) with 10% palladium on carbon (50 mg.) showed that the first mole of hydrogen was absorbed in one hour and the second mole in another 3 hours. On working up the reduction product, followed by evaporative distillation, there was obtained an oil (95 mg.), b.p 110-15°/0.2 mm, n_D^{25} 1.4980. (Found: C, 82.64; H, 11.62. $C_{19}H_{32}O$ requires C, 82.61; H, 11.59%). The same pair of isomeric 2:4-dinitrophenylhydrozones were obtained from this oil, identified by the determination of the mixed m.p.

$LiAlH_4$-*reduction of the Ketones* (I & II).—To a slurry of $LiAlH_4$ (150 mg.) in dry ether (15 c.c.) was added a solution of the unsaturated ketone (850 mg.) in dry

ether (60 c.c.). The reaction was allowed to proceed at room temperature for 24 hours. After addition of cold ammonium chloride solution, the aqueous layer was extracted thoroughly with ether. The combined ether extract was washed with cold water and then dried over a mixture of anhydrous sodium sulphate and potassium carbonate. The solvent was removed and the residue (750 mg.) on first evaporative distillation furnished an oil (700 mg.), b.p. 120°/0.1 mm, λ_{max} 250 mμ (ε 800), λ_{max} 284 mμ (ε 150) which on three similar distillations afforded an oil (600 mg.), b.p. 120-25°/0.1 0.15 mm, λ_{max} 275 mμ (ε 1,250) and 284 mμ (ε 1,280). (Found: C, 84.02; H, 10.82. $C_{19}H_{30}O$ requires C, 83.21 ; H, 10.95%).

The Mixture of 2 : 4b-*Dimethyl*-1 : 2-cyclo*pentano*-1 : 2 : 3 : 4 : 4a : 4b : 5 : 6 : 7 : 8 : 8a-*decahydrophenanthrene* (IX) *and* 2 : 4b-*Dimethyl*-1 : 2-cyclo*pentano*-1:2:3:4 : 4a:4b:5:6:7:8-*decahydrophenanthrene* (VIII).—A mixture of the aforementioned reduction product (750 mg.) in benzene (15 c.c.) and *p*-toluenesulphonic acid (100 mg.) was refluxed under an atmosphere of nitrogen for 1 hour. The cooled reaction mixture was washed with a solution of sodium bicarbonate and water. After evaporation of the solvent, the residual straw-yellow liquid (620 mg.) was evaporatively distilled to furnish a light yellow-coloured oil, b.p. 115°/0.15 mm, λ_{max} 254 mμ (ε 6,200) and 285 mμ (ε 8,900), n_D^{26} 1.5519. (Found : C, 88.23 ; H, 10.55. $C_{19}H_{28}$ requires C, 89.06 ; H, 10.94%) (cf. Braude and Wheeler, *loc. cit.*). This mixture of dienes was found to turn black very rapidly during distillation with the deposition of black particles, but when distillation was carried out under an atmosphere of nitrogen, the mixture did not turn black for a comparatively long period.

Maleic Anhydride Adduct.—A solution of the freshly distilled mixture of dienes (VIII and IX, 500 mg.) and freshly sublimed maleic anhydride (200 mg.) in xylene (2 c.c.) was refluxed under nitrogen atmosphere in an oil-bath (140°) for 8 hours. After allowing the reaction mixture to stand at room temperature overnight, the solvent was removed by warming under suction. The residue was taken up in ether and the ethereal solution on evaporation furnished a slightly coloured solid (500 mg.), m.p. 136° with adhering oil, which was transferred to a filtering arrangement and the oily portion was separated by suction. The solid material was washed with a small amount of petroleum ether (60-80°). The solid material (200 mg.) could neither be crystallised nor purified by chromatography due to separation of a further oily material on each attempt for purification. The crude solid material, m.p. 146-47° (100 mg.), was heated with distilled aniline (0.5 c.c.) on the steam-bath for 15 mins. The semisolid product, thus obtained, was triturated with cold dilute hydrochloric acid, when a crystalline material (50 mg.) separated out. Four crystallisations from dilute ethanol (1 : 1) furnished colorless fine needles, m.p. 194-96°. (Found : C, 81.01 ; H, 8.57. $C_{29}H_{35}O_2N$ requires C, 81.08 ; H, 8.21%).

The oil, obtained after separation of the crude adduct, was evaporatively distilled at 120-25°/0.2 mm under nitrogen atmosphere to afforded an oil, λ_{max} 253 mμ (ε 10,000) and 285 mμ (ε 6,100).

2 : 4b-*Dimethyl*-1 : 2-cyclo*pent*-$\Delta^{1:1}$-1:1'-*eno*-1 : 2 : 3:4:4a:4b:5:6:7:8:8a : 9-*dodecahydrophenanthrene* (X).—(*a*). A mixture of the reduction product (400 mg.) and fused powdered potassium hydrogen sulphate (1 g.) was heated under an atmosphere of nitrogen

at 170-80° under reduced pressure for 1 hour. The cooled reaction mixture was worked up with ether. The ethereal extract was washed successively with water, sodium bicarbonate solution and water, and dried over anhydrous sodium sulphate. After removal of of the solvent, the residue was evaporatively distilled to yield a slightly straw-coloured oil (200 mg.), b.p. 130°/0.2 mm, n_D^{25} 1.5395, λ_{max} 245 mμ (ε 8,500). This diene was more stable than the aforementioned mixture. (Found: C, 88.60; H, 10.63. $C_{19}H_{28}$ requires C, 89.06; H, 10.94%).

(*b*). The aforementioned mixture of dienes (VIII and IX, 800 mg.), on similar treatment with fused potassium hydrogen sulphate, furnished an oil (400 mg.) which was evaporatively distilled, b.p. 128-30°/0.2 mm, n_D^{25} 1.5396, λ_{max} 244 mμ (ε 8,500). (Found: C, 88.86; H, 10.73. $C_{19}H_{28}$ requires C, 89.06; H, 10.94%).

(*c*). A mixture of the solution of the diene (X, 100 mg.) in dry benzene (5 c.c.) and *p*-toluenesulphonic acid (50 mg.) was refluxed under nitrogen atmosphere for one hour. On working up, the residue on evaporative distillation furnished an oil (50 mg.), b.p. 130-35°/0.2-0.3 mm, n_D^{25} 1.5395; λ_{max} 245 mμ (ε 8,500).

2:4b-*Dimethyl*-1:2-cyclo*pentano*-1:2:3:4:4a:4b:5:6:7:8:8a:9:10:10a-*tetradecahydrophenanthrene* (XI).—(*a*). A solution of the diene (X, 300 mg.) in ethanol (50 c.c.) was hydrogenated in presence of 10% palladium on carbon (100 mg.). Two moles of hydrogen were absorbed during 48 hours. On working up and on evaporative distillation there was obtained a colorless oil (270 mg.), b.p. 1 0-25°/0.1-0.15 mm, n_D^{25} 1.5398. (Found: C, 87.88; H, 12.32. $C_{19}H_{32}$ requires C, 87.69; H, 12.31%).

One drop each of the diene (X) and the above-mentioned saturated hydrocarbon (XI) was treated with a drop of tetranitromethane (Feiser, "Experiments in Organic Chemistry", 3rd. ed., pp. 71-72) on the filter paper. The portion treated with diene developed yellow stains but that treated with the saturated hydrocarbon (XI) did not develop any stain.

(*b*). The mixture of the dienes (VIII and IX, 270 mg.) in ethanol (70 c.c.) was hydrogenated in presence of the above catalyst (100 mg.), when one mole of hydrogen was absorbed in 10 minutes and the second mole in 5 hrs. On evaporative distillation, a transparent oil (220 mg.) was obtained, b.p. 120-25°/0.1 mm, n_D^{30} 1.5141. (Found: C, 87.46; H, 12.26. $C_{19}H_{32}$ requires C, 87.69; H, 12.31%). This saturated hydrocarbon, also, did not respond to tetranitromethane test.

(*c*). Two moles of hydrogen were absorbed by the mixture of dienes (VIII and IX, 250 mg.) when hydrogenation was carried out in glacial acetic acid (15 c.c.) in presence of platinum oxide (50 mg.). The hydrogenation product was evaporativly distilled to furnish the same oil (230 mg.), b.p. 125-30°/0.2 mm, n_D^{32} 1.5150.

Perbenzoic acid in 5.36% $CHCl_3$ solution had no action on the saturated hydrocarbons [XI, described under (*a*) and (*b*) above] in $CHCl_3$ solution, when kept for 18 hours at 26-30°.

3′-*Methyl*-1:2-cyclo*pentenophenanthrene*.—The dienes (VIII, IX and X; 440 mg.) was dehydrogenated with 30% palladium on charcoal (300 mg.) at 320-40° (bath temperature) for 3 hours in a Heymann apparatus while a slow stream of nitrogen was allowed to pass through the apparatus. The product was extracted with ether. The ethereal solution, which showed fluorescence, was evaporated on a steam-bath and the

residue, on evaporative distillation at 150-55°/0.2 mm, furnished a yellow solid (25 mg.), m.p. 120-30°. The latter was crystallised three times from ethanol, m.p. 146-47° (cf. Cook and Hewitt, *J. Chem. Soc.*, 1933, 1099). This meterial (20 mg.) was chromatographed on alumina (2 g.), using petroleum ether (60-80°) as the eluting solvent, when crystals (12 mg.), m.p. 125-26°, were obtained. The melting point did not rise on crystallisation from ethanol. To a hot solution of this material (10 mg.) in benzene (5 c.c.) was added a hot saturated solution of *s*-trinitrobenzene (10 mg.) in a mixture of ethanol and benzene (1 : 1), when the complex crystallised out (10 mg.), m.p. 144-46°. Seven crystallisations from the above solvent mixture furnished yellow needles, m.p. 146-47° (3 mg.) (Kon and Ruzicka, *ibid.*, 1934, 124; Cook and Hewitt, *loc. cit.*; Bergmann and Bergmann, *loc. cit.*; Gamble and Saunders, *ibid.*, 1935, 644). (Found: N, 9.52. Calc. for $C_{24}H_{19}O_6N_3$: N, 9.44%).

9-*Keto*-2-*methyl*-1 : 2-cyclo*pentano*-1 : 2 : 3 : 4 : 4a : 4b : 5 : 6 : 7 : 8 : 8a : 9 : 10 : 10a-*tetradecahydrophenanthrene* (XIII).—A solution of (XII, m.p. 95-96°; Banerjee *et al.*, *loc. cit.*, 180 mg.) in ethanol (25 c.c.) was hydrogenated over 10% palladium on carbon (100 mg.). One mole equivalent of hydrogen was absorbed in course of 6 hours. The reduction product was worked up to afford an oil (180 mg.), which on evaporative distillation at 100-105°/0.15 mm furnished silky needles (160 mg.), m.p. 68-70°, on standing. This was crystallised twice from petroleum ether (40-60°) to furnish white needles (140 mg.), m.p. 73-74°. A sample of the reduced product was admixed with a sample of the saturated ketone, m.p. 73-74°, obtained by the lithium and ammonia reduction of the unsaturated ketone (XII), and the mixed melting point remained undepressed. The identity of the two products was further proved by comparing their 2 : 4-dinitrophenylhydrazones.

Preparation of the Diene from (XII).—To a slurry of $LiAlH_4$ (200 mg.) in dry ether (20 c.c.) was added a solution of the unsaturated ketone (XII, 600 mg.) in dry ether (40 c.c.). The reaction was allowed to proceed at room temperature for 24 hours. The cooled reaction mixture was worked up, as described before, to afford an oil (500 mg.) which was transferred to a fractionating Claisen flask with dry benzene (50 c.c.). *p*-Toluenesulphonic acid (20-30 mg.) was added to the benzene solution and the reaction mixture was slowly distilled, when during 1 hour the distillate (20 c.c.) was collected. The content of the flask was transferred into a separating funnel which was washed with sodium bicarbonate solution and water. The solvent was removed to yield an oil (400 mg.) which was evaporatively distilled thrice to furnish a light yellow oil (200 mg.), b.p. 90-95°/0.15 mm, λ_{max} 245 mμ (ε 13,800), n_D^{31} 1.5513. A considerable portion of the oil polymerised during distillation. (Found: C, 89.23; H, 11.06. $C_{18}H_{26}$ requires C, 89.25; H, 10.74%).

The following experiments were carried out with the oil, obtained after chromatographic separation and crystallisation of the unsaturated ketone (XII).

The first few oily fractions of chromatography (800 mg.) together with the oil (100 mg.), obtained after separation of the solid (XII), were combined and the combined oil was evaporatively distilled to furnish a yellow oil (500 mg.), b.p. 106-10°/0.1 mm, which after three subsequent distillations at the same temperature afforded a material

having λ_{max} 252 mμ (ε 3,160), n_D^{30} 1.5239. (Found : C, 78.06 ; H, 10.15%). This oil did not yield any solid semicarbazone or 2 : 4-dinitrophenylhydrazone. A portion of the aforementioned oil (200 mg.) and fused and powdered potassium hydrogen sulphate (1 g.) were heated at 160-70° (bath temp.) under water suction and nitrogen atmosphere for 30 mins. The cooled reaction mixture was worked up with ether, the ethereal solution was washed successively with water, sodium bicarbonate solution and water, and dried over anhydrous sodium sulphate. After removal of the solvent the residue was evaporatively distilled to yield a slightly yellow oil (100 mg.), b.p. 140-45°/0.2 mm, λ_{max} 254 mμ (ε 3,240) and 278 mμ (ε 3, 700). (Found : C, 79.51 ; H, 8.46%).

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SYNTHESIS OF SUBSTITUTED AROYLBENZOFURANS. PART II

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Several aroylbenzofurans and naphthofurans have been synthesised by the Rap reaction, using *o*-hydroxyaldehydes.

In continuation of our work on this subject (this *Journal*, 1958, **35**, 136), the present investigation reports the synthesis of ten aroylbenzofurans by the Rap reaction, using *o*-hydroxyaldehydes instead of *o*-hydroxyketones. In all, five *o*-hydroxyaldehydes have been condensed with ω-bromoacetophenone and ω-bromo-*p*-chloroacetophenone.

o-Hydroxyaldehydes required in the synthesis were obtained by an improved general procedure for the Duff reaction (*J. Chem. Soc.*, 1941, 151), as advocated by Liggot and Diehl (*Proc. Iowa Acad. Sci.*, 1945, **52**, 191) using different phenols, e. g., *p*-cresol, 2-chloro-4-butyl^t-, *p*-hydroxydiphenyl- and *p*-chloro-phenols.

The 2-aroylbenzofurans and naphthofurans were characterised by the preparation of different carbonyl derivatives. Alcohol-soluble benzofurans were characterised by the preparation of either the oximes or semicarbazones, while the *p*-nitro- or the 2 : 4-dinitro-phenylhydrazone was used for the characterisation of alcohol-insoluble compounds.

Red halochromy with concentrated sulphuric acid, as reported by Buu Hoï *et al.* (*J. Chem. Soc.*, 1955, 3688), was also exhibited by most of the compounds reported herein (Table I).

Experimental

o-Hydroxyaldehydes of *p*-cresol, 2-chloro-4-butyl^t-, *p*-hydroxydiphenyl- and *p*-chlorophenols were prepared by an improved general procedure of the Duff reaction (*loc. cit.*).

Aroylbenzofuran and/or aroylnaphthofuran was prepared by the usual method used for the Rap condensation.

Carbonyl Derivatives.—The oximes, semicarbozones, *p*-nitro- and 2 : 4-dinitrophenylhydrazones, used for characterisation of the aroylbeozofurans and naphthofurans, were prepared by the usual methods.

TABLE I

No.	Benzofuran.	Cryst. from.	M.P.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.	Colour developed (Benzofuran + conc. H_2SO_4).	Carbonyl derivative.	M.P.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.	% Nitrogen. Found.	% Nitrogen. Calc.
1.	5-Methyl-2-*p*-chlorobenzoyl-	95% EtOH	148°	70.26	70.98	4.01	4.06	Blood-red	Oxime	168°	66.86	67.24	4.01	4.20	4.26	4 90
2.	5-Methyl-2-benzoyl-	Do	89°	79.84	81.35	5 24	5.08	Red	Semicarb.	178°	69.02	69.61	5.00	5.12	14.01	14.33
3.	2-*p*-Chlorobenzoyl-naphthofuran	Do	154°	74.81	74.39	3.20	3.59	,,	D.N.P.	>265°	61.11	61.67	2.92	3.08	11.02	11.51
4.	2-Benzoyl-naphthofuran	Trituration with MeOH	101°	83.02	83.81	4.01	4.41	,,	Semicarb.	198°	72.15	72-95	4 14	4.56	12.15	12.76
5.	5-butyl'-7-chloro-2-*p*-chlorobenzoyl-	Gl. acetic acid	130°	65.11	65.70	4.15	4.61	Deep orange	D.N.P.	>300°	56.21	56.92	3.23	3.79	10.17	10.67
6.	5-butyl'-7-chloro-2-benzoyl-	95% EtOH	105°	72.16	72.95	5.13	5.44	Deep brown -yellow	Semicarb.	236°	64.21	64.66	5.17	5.41	11.02	11 37
7.	5-Phenyl-2-*p*-chlorobenzoyl-	Gl. acetic acid	164°	75.18	75.80	3.27	3.91	Orange	N.P.	...	69.01	69.30	3.91	3.85	8.27	8.98
8.	5-Phenyl-2-benzoyl-	95% EtOH	80°	84.01	84.55	4.15	4.69	Red	Semicarb	155°	74.02	74.36	4.82	4.79	11 85	11.83
9.	5-Chloro-2-*p*-chlorobenzoyl-	Benzene	185°	61.30	61.85	2.26	2 75	Deep orange	N.P.	258°	58.82	59.15	3.11	3.05	9 15	9.86
10.	5-Chloro-2-benzoyl-	Trituration with MeOH	138°	70.01	70.18	3.03	3.518	Yellow	Semicarb	165°	60.76	61.24	3.95	3.83	13.11	13.40

N:P and D.N.P. denote respectively *p*-nitrophenyl- and 2:4-dinitrophenyl-hydrazone.

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SHORT NOTES

STUDIES ON THE METAL COMPLEXES OF HYDROXAMIC ACIDS. COLOURED COMPLEXES OF IRON, VANADIUM AND MOLYBDENUM WITH *iso*NICOTINOHYDROXAMIC ACID AND THEIR ANALYTICAL USES

By R. L. Dutta

In continuation of the previous work on the use of pyridine hydroxamic acids (Dutta, this *Journal*, 1957, **34**, 311 ; 1958, **35**, 243) as colorimetric reagents for metals, a study of *iso*nicotinohydroxamic acid is now presented. This reagent behaves more or less like nicotinohydroxamic acid. The salient points of the conditions of the estimation and the empirical composition are also recorded. Preparation of the reagent and of the metal solutions and the instruments used for the measurement of optical density and of *p*H were the same as described earlier.

Determination of Iron.—Ferric iron produces three coloured complexes: violet (abs. max. 490 mμ ; *p*H 1.5) ; wine-red (rather unstable ; abs. max. 460-480 mμ ; *p*H 2.5-2.9) and golden yellow (abs. max. 440 mμ ; above *p*H 4.0). The last colour reaction is sensitive and useful for spectrophotometric determination of traces of iron over the *p*H range of 4.5 to 6.2. Ferrous iorn produces only a golden yellow colour, which appears to be the same as that formed with ferric iron. Thus, this golden yellow colour can be utilised for the determination of iron, irrespective of the valency state of the metal.

The golden yellow-coloured complex obeys Beer's law over the range 0.5γ to 8γ Fe/c.c. The sensitivity is 0.014 Fe/cm^2 (Sandell) for ferric as well as for ferrous iron.

Interference caused by small amounts of titanium, uranium and molybdenum may be eliminated by measuring the optical density at 520-530 mμ instead of at 440 mμ, because at these wave lengths the absorption of the other coloured species is negligible. But serious interference is caused by oxalate, citrate and vanadium.

The empirical compositions have been determined by Job's method of continued variation as described earlier. Violet complex, 1 : 1 ; golden yellow complex, 1 : 3.

Determination of Vanadium.—The reagent develops with vanadate a series of colours : in aqueous medium—bluish purple (abs. max. 500 mμ) in acid region, purple (abs. max. 500-510 mμ) in weakly alkaline medium ; in 50% ethanol—there appears a brownish yellow colour (no abs. max. in the visible) in acid medium and a purple colour (abs. max. 500-520 mμ) at *p*H 7.6-7.8. The brownish yellow colour in 50% ethanol offers a rather wide range of *p*H 2.5 to 3.9 for colorimetric determination of vanadium. Nicotinohydroxamic acid (*loc. cit.*), on the other hand, produces in 50% ethanol and in acid range, a bright golden yellow colour with a distinct abs. max. at 440 mμ.

Optical density of the brownish yellow colour was measured at 440 mμ. Beer's law is obeyed over the range 1γ to 8γ V/c.c. and sensitivity is 0.012 V/cm² (Sandell). In presence of small amounts of titanium, uranium and molybdenum, optical density measurements are to be made at 510-520 mμ. But iron and citrate ions cause serious interference.

All the coloured complexes in aqueous as also in 50% ethanol media are found to be 1 : 3 complexes.

Determination of Molybdenum.—Molybdate produces a yellow colour with the reagent which has no absorption maximum in the visible. Optimum *p*H for the development of the coloured complex lies within the range of 6.5 to 7.8, and measurements may be made at 380-390 mμ. As the reagent solution has a slight absorption under the conditions, measurements should be made against the reagent blank. Beer's law is followed over the range 4γ to 20γ Mo/c.c. Most of the common ions interfere. Empirical composition of the complex is 1 : 2.

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THERMOMETRIC STUDIES ON THE COMPOSITION OF CADMIUM ARSENITE COMPLEXES

By M. S. Bhadraver and J. N. Gaur

There are very few references in literature to the study of cadmium arsenite by applying physico-chemical methods. According to Reichard (*Z. anal. Chem.*, 1898, **37**, 749) $Cd_2As_2O_5$ is formed by adding acid potassium arsenite to the solution of cadmium sulphate and reprecipitating with sodium meta-arsenite. If sodium ortho-arsenite is added to a cadmium salt, cadmium diarsenite, $3CdOCd_2As_2O_5.2H_2O$, is precipitated. In view of the difficulties associated with analytical work and in the absence of any decisive views on the composition of these complexes, it was considered worthwhile to study the composition of these complexes by physico-chemical methods.

E. Merck samples of $2CdCl_2.5H_2O$ and sodium arsenite were taken. Using different concentrations of the two salts in solution, the titrations were followed both by the direct and reverse methods. The titrations were also carried out in presence of alcohol up to a total concentration of 20% by volume. The total rise in temperature was then plotted against the titre in c.c. and the equivalence point was noted by the intersection of the two curves.

The mechanism of the reaction in the direct and reverse thermometric titrations can be visualised as follows:

$$CdCl_2 + 2NaAsO_2 = Cd(AsO_2)_2 + 2NaCl.$$

The possibility of the reaction according to the following equation can be ruled out on the basis of the absence of H_3AsO_3 in the reaction mixture and on the percentage of cadmium in the complexes formed.

$$2CdCl_2 + 4NaAsO_2 + 3H_2O = CdOCd(AsO_2)_2 + 4NaCl + 2H_3AsO_3$$

The percentage obtained from analytical study of the product corresponds to the formula $(AsO_2)_2Cd$ and not $CdOCd(AsO_2)_2$. It was also observed that in all titrations, a white precipitate was first formed which did not change in colour on further addition of titre in each case, but the precipitate became more dense. The direct thermometric titration curves yield one point of equivalence in the ratio of 1 : 2 (Cd:As), indicating the formation of $Cd(AsO_2)_2$. The reverse titration curves indicate the formation of the same complex $Cd(AsO_2)_2$ in the ratio of 2 : 1 (As:Cd).

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ACTION OF BROMINE ON 2:6-DINITROHYDROQUINONE-4-ACETATE. A NEW FORMATION OF TETRABROMO-*p*-BENZOQUINONE

By J. Schawartz*

It is a well-known phenomenon, that interaction of bromine and nitric acid on various substituted or unsubstituted benzene derivatives results in the formation of tetrabromo-*p*-benzoquinone (I). The only previously nitrated compound, *p*-nitrophenol, was obtained by Datta and Chatterjee (*J. Amer. Chem. Soc.*, 1923, **45**, 480) and was converted to (I), although in the presence of nitric acid. In our case, 2:6-dinitrohydroquinone-4-mono-acetate (II) (for preparation vide Nietzki, *Ber.*, 1878, **11**, 470; Semplen and Schawartz, *Acta chim. Acad. Sci., Hung.*, 1953, **3**, 490) was brominated with bromine, and after a short time (I) was formed in a good yield.

A solution of 2:6-dinitrohydroquinone-4-mono-acetate (2.42 g., 0.01*M*) in 15 c.c. of glacial acetic acid was refluxed with bromine (6.4 g., 0.08 atom) for 3 hours and irradiated during this time with a mercury lamp. After refluxing, the yellow crystals containing the mixture was poured into 120 c.c. of cold water. The crystals were collected on a glass-filter, washed with water and dried in vacuum at 30°; yield of (I), 3.72 g. (88.4%), m.p. 296°. This substance is free from nitrogen. It was once recrystallised from dioxane, m.p. 300°; it gave no depression with an authentic sample. (Found: Br, 75.2. Calc. for $C_6O_2Br_4$: Br, 75.5%).

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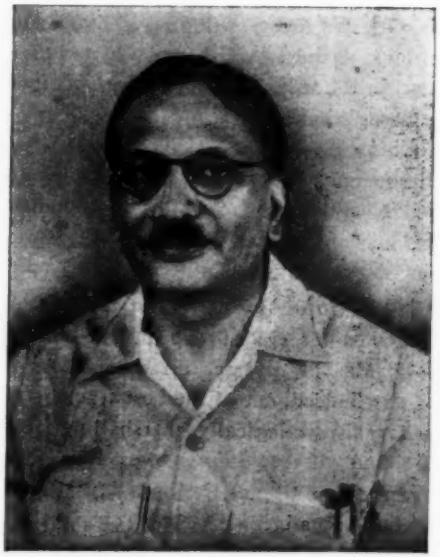
OBITUARY

Jnan Chandra Ghosh

Born : Sept. 4, 1894. Died : Jan. 21, 1959.



It is with profound regret that we place on record here the sudden demise of Jnan Chandra Ghosh on January 21, 1959, at his Calcutta residence. He was a founder member of this Society as also one of its past president. He was only 64 at the time of his death.

Jnan Chandra was born at Purulia on Sept. 4, 1894. After passing his entrance examination from the Giridih High School (1909), he entered the Presidency College, wherefrom he obtained his M.Sc. degree in 1915, standing first in First Class, and won a number of medals. It was during his student days at the Presidency College that he came in intimate contact with his illustrious *Guru*, Acharyya Prafulla Chandra Rây, a contact which contributed greatly in shaping his future career. Inspired by his teacher, he almost immediately devoted his whole attention to research work. His early investigations were carried out in the Presidency College laboratory, but soon after, he was appointed a lecturer in chemistry in the newly founded University College of Science, Calcutta.

The first important work which evoked world-wide interest resulted in the Ghosh's theory of abnormal behaviour of strong electrolytes (1918). This was a venture in a completely unknown domain and, indeed, threw a new light on the subject. The postulates of the theory had later on been modified and replaced by more apt ones, but, nevertheless, Ghosh showed the way how such a problem had to be tackled. Late Dr. Shanti Swarup Bhatnagar in his presidential address to the chemistry section of the Indian Science Congress in 1928, referred to Ghosh's dilution theory in the following words:

"Ghosh's Theory (1918) on the abnormality of strong electrolytes created a stir in the scientific world when it first made its appearance. The hypothesis of complete dissociation of strong electrolytes postulated by Sutherland, Bjerrum and Milner had prepared the field for a warm reception of a theory of complete dissociation. Milner's treatment of his theory was extremely logical but he failed to demonstrate its advantages and the advanced mathematics involved deterred many chemists from attacking the

subject. The clarity with which Ghosh demonstrated the superiority of his hypothesis over the ideas current at the time received for it a ready acceptance from such distinguished scientists as Planck, Nernst, Sir James Walker and G. N. Lewis. The theory has been subjected to a very adverse critism by Kendall and Partington on account of certain apparent defects in the mathematical presentation ... ... Theories come and go but good ones always open up new fields of research and lead to the consolidation of the ground already covered. From that standpoint, Ghosh's theory will always live, as it has undoubtedly introduced a change in scientific thought and established the hypothesis of complete dissociation as far as strong electrolytes are concerned. Debye gave a better mathematical treatment of the theory of complete dissociation in 1923."

He was awarded D.Sc. degree on his work (1918) by the Calcutta University. Dr. Ghosh was also the recepient of the Premchand Roychand studentship of the same University with which he proceeded to England (1919) to work under Professor Donnan. Subsequently he went over to Germany and carried out some work there under Professors Nernst and Haber who showed great interest in his work.

On his return to India in 1921, he joined the Dacca University as the Professor and Head of the Department of Chemistry. Then followed an era of one decade and a half of ebullient activities, which revealed his talents in diverse directions. As a professor he earned the greatest reputation and he was, indeed, one of the best teachers of this country. He was a polished and refined speaker, always logically marshalling facts in a convincing fashion to keep the listeners spell-bound whether in a class-room or on a public platform. Equally remarkable were his research activities in those days, when hosts of scholars gathered around him and he soon built up a brilliant school of physical chemistry.

Dr. Ghosh's contributions to fundamental knowledge cover a wide field :- electrochemistry, kinetic studies, fluorescence, catalysis, auto-oxidations and other allied branches, but the most intensive works were carried out in the field of photochemistry. The investigations of the kinetics, the photosensitivities, the quantum efficiencies of photochemical reactions with innumerable homogeneous and colloidal systems, using both polarised and non-polarised radiations, revealed a wealth of information regarding the mechanism of such changes. Studying with *d*- and *l*-circularly polarised light, he was led to the circular dichroism of photocatalysts which due to pre-excitation in ultraviolet light assumed anisotropy. These observations are of considerable importance and promise far-reaching developments. In addition to these investigations, he also carried out a good deal of work in another branch, viz., that of technical gas reactions to which we shall refer later. Indeed, research was the foremost passion of his life and though he held many administrative positions in later periods, his keen interest in research and his contributions continued right up to the end of his life.

At Dacca, he was also intimately connected with innumerable administrative bodies of the University besides holding the office of the Provost of the Dacca Hall (1925-1939). Simultaneously he was associated with many organisations for scientific research or developments of Science, e.g., Council of Agricultural Research, Indian Science Congress Association, Institute of Sciences, Journal of the Indian Chemical

Society, Science & Culture etc. He was elected the General President of the Indian Science Congress in 1939 at Lahore. Everywhere he made his presence felt by his sound constructive suggestions, hard work and his unique pursuasive methods. As a provost he came in close contact with generations of students and had a first-hand knowledge of their problems and their psychology. His dealings with students were so sympathetic and forbearing that it was difficult to judge whether the universal esteem that he enjoyed was more as a professor or as a friend and guide of students.

In 1939, he was summoned away to Bangalore as the Director of the Indian Institute of Science in succession to Sir C. V. Raman. Keenly alive to the inescapable developments of modern times, that science and technology are the dispensers of the gifts of progress, he devoted himself with ardent zeal to the development of the Institute with the special aim of training up young engineers and scientists Various new developments like power engineering, aeronautical engineering, internal combustion engineering, fermentation technology, high pressure technology, etc., were introduced. That the Indian Institute of Science at Bangalore holds such an eminent position to-day in the field of higher engineering education and research, is largely due to the ceaseless and indefatigable work and foresight of Dr. Ghosh.

In spite of the heavy pressure of administrative work, he relentlessly pursued his researches which were then switched on to the new field of technical gas reactions, suited to industrial problems. The rudiments of this work were started at Dacca where he attempted the development of the Fischer-Tropsch process for synthesis of liquid fuels. His discovery of a catalyst of iron-copper, promoted by traces of nickel, thoria and ceria, proved to be of immense value in Japan. With a brilliant band of workers, trained by him, he made a thorough investigation of the possibilities of synthesising liquid fuels from cheap sources, using diverse types of catalysts. This development offers great possibilities not only for the production of synthetic fuels but also as a source of raw materials for a variety of chemical products like wax, fat, plastic, rubbers, etc. In addition, his fundamental work on adsorption of gas on catalysts of technical importance has earned him a great name abroad. In the field of technical gas reactions and high-pressure technology, Dr. Ghosh had been the pioneer in this country. The results of his interesting work in this line have been incorporated in the volume of the masterly treatise 'Some Catalytic Reactions of Industrial Importance' written by Dr. Ghosh in collaboration with Dr. S. K. Bhattacharyya and Dr. M. V. C. Shastri.

It was a trait of his character to make the quick and best use of all available resources. He also possessed the capacity for making lightning decisions backed up by rock-like faith and firm convictions. Ever since he came in contact with his guru, Acharyya Ray, he was conscious of the necessity of development of national industries which would be a panacea for mitigating the appalling poverty of the Indian masses. In recognition of his service to the cause of chemical research and chemical education, Knighthood was conferred on him in 1943.

When he was busy in investigations of Indian raw materials for development of industries, specially to produce urea and phosphatic fertilisers, synthetic rubber, titanium dioxide, carbon disulphide etc., he was called away to Delhi to function

as the Director General of Industries & Supplies (1947-1950). It was a heavy burden, but he piloted in those critical days the industrial schemes in collaboration with European and American experts for not only the steel and heavy chemical industries but also he initiated the basis of the petroleum and petroleum refining industries, the machine tool industries, cable industry, wireless equipment and radar industry etc. Simultaneously he acted as a Member of the All-India Council of Technical Education and as the President of Principals of Technical Institutions in India. He lost no time in translating into action his ideas and, while formulating the policy of the Government in these matters, he keenly felt the lack of adequately trained personnel needed in large-scale improvement of industrial undertakings. Thus originated, through his vision and foresight, the necessity of starting technological institutes in the country, and he did lose no moment in starting the first one of its kind at Kharagpur in 1950, financed by the Government of India. He accepted the office of the Director of the Institute willingly and worked hard for four years in establishing the Institute on a firm basis ; the Institute remains a fitting memorial to the constructive genius of Dr. Ghosh. In 1954, at a critical stage in the educational life of Bengal, he was called upon to shoulder the responsibility of the Vice-Chancellorship of the Calcutta University, which he readily accepted. If research was the first passion of his life, the well-being of the students was the next consuming passion in him. One of the first acts of his as the Vice-Chancellor was to make a survey of the living conditions and educational amenities of the students of colleges and the University. He drew the attention of the Government and the country to the colossal waste of intellect and manpower due to neglect in maintenance of prequisites for adequate education. It was his habit always to go deep into every matter he took up and never waste a moment to start the work. He immediately proceeded with his schemes, but only a few months later he was taken away from the University to serve more important a purpose, namely, to act as a Member of the Planning Commission. This office he held till his last breath.

It was during his tenure of office as the Vice-Chancellor and a Member of the Planning Commission, that we saw the great educationist and humanist in him. Thoroughly conversant as he was with the academic world, with his wide vision he succeeded in formulating the fundamentals of the entire educational systems of independent India. Zealously wedded to science, he was a firm believer in technological development, but he was never parochial and repeatedly cautioned the country against the neglect of literature and humanities. His countless speeches and convocation addresses will bear testimony to this.

A dauntless fighter for the development of education, the advancement of scientific knowledge in this country, the welfare of students and the uplift of the masses, he would not hesitate a moment to undertake any work, however strenuous the toil it might involve. He worked ceaselessly and selflessly as he used to say, 'hard and selfless work can only save this country.' To the students he was not only a very able guide but also a sincere friend. He was the fountain-head of inspiration to innumerable institutions and undertakings, which developed marvellously under his loving care.

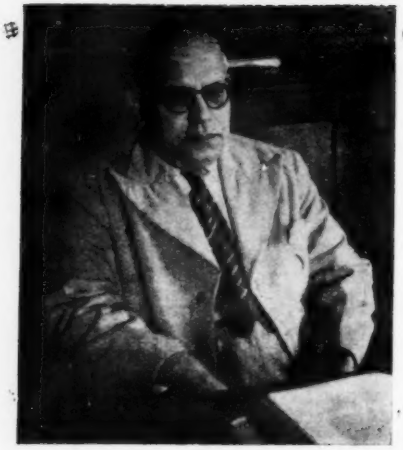
He used to say often, 'I would like to work till my last breath and the moment I would cease to work I wish to leave this world'. Indeed, it is literally true and his desire is fulfilled. A rare combination of knowledge, tolerance, and philosophical equanimity radiated from Ghosh, making every contact with him a pleasant and fruitful experience. The modesty, large heartedness and helpfulness of this exceptional man were simply admirable.

In the history of the constructive development of this country, the name of Jnan Chandra is written in indelible letters. He was an eminent professor, a splendid administrator and a great man.

P. C. Rakshit.

Biman Bihari Dey

Born: Nov. 1, 1889. Died: Jan. 18, 1959.



In the death of Dr. Biman Bihari Dey the Indian Chemical Society has lost one of its most distinguished Foundation Fellows and a past President, who also served the Society in several other capacities till the end of his life. He was one of the seniormost Fellows, who was held in great esteem and regard by all connected with the Society for his pioneering contribution to the development of chemical research and education in India, as well as for his wise counsels and dignity of character.

Biman Bihari Dey was born at Calcutta on November 1, 1889. He was the youngest son of Bhai Kedarnath Dey, then a leading missionary of the New Dispensation Order of the Brahmo Samaj, founded by Brahmananda Kesab Chandra Sen. His father had to maintain a large family with modest means, and young Dey had not an easy and smooth life to begin with. With limited family resources Dey could not afford to buy many of the text-books which he required for his study. But with a calm and resolute mind, undaunted by circumstances, he went through his career with an unflagging zeal. There is little doubt that Dey inherited his strength of mind together with his religious temperament and spirit of detachment, so well revealed in later life, from his pious father.

Dey had his early education in the City Collegiate School, Calcutta, from where he passed the Entrance Examination (equivalent to Matriculation or the present School Final Examination) in 1904. In 1906 he passed the First Examination in Arts (corresponding to the present I A. and I.Sc. examinations) from the City College, Calcutta. He obtained the B.Sc. degree of the Calcutta University in 1908 from the Presidency College, Calcutta, with honours in both chemistry and botany. In 1910 he gained the M. Sc. degree of the University in chemistry from the same college. It was in the post-graduate M.A. and M.Sc. class of the Presidency College that the present writer came in contact with Dey and cultivated a close friendship with him. By its constancy of affection, sincerity of purpose and counsel of wisdom this friendship often aided the writer in later life to invigorate his spirit and balance the vicissitudes of years. A few years later Dey earned the distinction of winning the Premchand Roychand Scholarship and Mouat gold medal of the University.

While a student in the City College, Dey came in close contact with his class-mate H. K. Sen (died in 1945), who subsequently distinguished himself as a great teacher and a pioneering worker in the field of Applied Chemistry in India. Their mutual

attachment grew with time in later years into an indissoluble bond of fast and abiding friendship. At the Presidency College, Dey had the unique opportunity of coming under the influence of that great teacher, Acharyya Prafulla Chandra Rây, who is rightly regarded as the Father of Indian Chemistry. It was mainly through his inspiration that both Dey and Sen imbibed a spirit of dedication to the career of a chemist.

Almost immediately after obtaining the M.Sc. degree, Dey joined the Scottish Churches College, Calcutta, as a lecturer in chemistry, but left it in August, 1911, when he proceeded to England for higher studies and research in chemistry. But even before he left for England, Dey carried out two small pieces of research in collaboration with H. K. Sen, which related to the interaction of nitrites with hydrazine sulphate. These were reviewed in the Annual Reports on the Progress of Chemistry for 1911 and 1912.

After his arrival in England, Dey entered the Imperial College of Science and Technology in London and worked in the laboratory of the late Professor Sir J. F. Thorpe. Here he was soon joined by his friend H. K. Sen in the following year. In 1912 Dey was awarded the Diploma of the Membership of the Imperial College of Science (D.I.C.) in recognition of his research activity, and in 1913 he passed the examination for the Associateship of the Institute of Chemistry, London (A.I.C., now A.R.I.C.). His first independent comprehensive research on coumarin condensation, embodied in a thesis, gained him the D.Sc. degree of the University of London in 1915. Besides his work for the D.Sc. thesis, Dey also made a few other publications while still working in London. In this connection mention may be made of his work carried out jointly with M. O. Forster on hydrazoximes of benzil and diacetyl.

Dey returned to India in 1915 and joined the Presidency College, Calcutta, in November 1916, as Professor of Chemistry in the I.E.S. in the place of his teacher Sir P. C. Rây who then retired to accept the Palit Professorship of Chemistry in the newly started University College of Science at the invitation of the late Sir Asutosh Mookerjee. Dey worked in the Presidency College, Calcutta, till April 1920, and in collaboration with his students carried out some researches which were published in the Journal of the Chemical Society, London. He then left for Madras to join as Professor of Chemistry in the I.E.S. at the Presidency College there, in the vacancy caused by the deputation of Dr. J. L. Simonsen, F.R.S. to the Munitions Board, Simla.

At the Madras Presidency College, Dey soon established his reputation as a very successful and inspiring teacher of chemistry, and ere long built up a flourishing school of research. During 1920-38, the period of his service as Professor of Chemistry there, Dey published in collaboration with his students a large number of original memoires, mostly in organic chemistry and some in bio-chemistry, and wrote the book, "Laboratory Manual of Organic Chemistry", in co-authorship with M. V. Sitharaman. It is now used as an authentic and standard text-book in the Indian Universities. Many of his students are now holding very high positions either as Professors of Chemistry in the Universities or as heads of chemical research laboratories in the country. It is, therefore, quite appropriate that he is regarded by many as "Father of Chemistry" in South India in analogy with the honour shown to his great teacher, Acharyya Prafulla Chandra Rây of illustrious memory.

Dey's publications in organic chemistry were made mostly on synthesis of coumarins and studies of their structures and reactions, on quinoline pyrones and their derivatives, on coumaryl-6-*iso*cyanates and -6-*iso*thiocynates and their reactions, on the influence of various negative groups in activating the halogen atom in the benzene nucleus, on the chemistry of natural products leading to the isolation of the alkaloids hedyotin from the roots of *Hedyotis auricularia*, todallin and toddallinin from the roots of *Toddalia aculcata* besides a lactone, toddallolactone, on the constitution of toddallolactone, on researches dealing with narcotine and cotarnine, on the *iso*quinoline ring system, on the preparation of various organic compounds by means of electrolytic oxidation and reduction, etc.

In the field of bio-chemistry, mention may be made of his work on the investigation of enzymes, known as peroxidases, on certain common Indian plants, on glandular products and on the preparation of hormones like pituitrin, thyroxin, insulin and adrenalin from the slaughter house refuse. It is of interest to note here that he supplied thousands of ampoules of pituitrin to the Director General, Indian Medical Service, during the second World War. Six patents were also taken for the manufacture of some of these gland products.

In 1927-28 Dey went out on a study tour to Germany and worked for some time in Berlin and Dahlem in bio-chemistry with Professors Pringsheim, Warburg, Lindner and Widenhagen. He also visited other centres of scientific research in Europe.

In 1938 Dey was appointed Principal of the Presidency College, Madras, which office he held till 1944. During the tenure of his service as Principal of the college he advocated the idea of building a women students' hostel, which was materialized just before his death, when the construction of the building was completed and it was opened formally by Dr. S. Radhakrishnan. Dey was indeed very happy that he lived to see it opened. A canteen for the students on the co-operative basis was also started in the college on his initiative during the period of his administration.

Dey retired in 1944 from his service in the Presidency College, Madras, on being appointed as the Director of Public Instruction there. He served in that capacity till 1946 and effected many improvements in the educational system of the province. It was through his earnest efforts that the healthy scheme of providing midday meals to the children in the corporation schools was introduced by the government.

Even after his retirement from the government service in 1946, Dey continued to carry on research activities by conducting various research schemes under the Council of Scientific and Industrial Research, Government of India, in the laboratory of the Presidency College, Madras, till 1948 when he was appointed Director of the Bio-chemistry Department of the University of Madras for the term 1948-50.

After leaving the university service Dey built up a laboratory in his own house at Santhome, Madras, in 1950-51, where he continued his work on the scheme of research on glandular products, which as stated above, was started earlier in the chemical laboratory of the Presidency College.

In January 1953 Dey was appointed Director of the newly started Central Electrochemical Research Institute at Karaikudi, South India. He guided the research and administrative work of this growing institution for about two years and then again

after an interval of a little over a year he was recalled to run the institute till the appointment of his successor in January, 1957. In spite of his failing health Dey spared no pains nor time and energy in building up that Institution into a fully equipped up-to-date centre of research in electrochemistry. Even within this short period of his administration no less than a dozen research publications were contributed by him in collaboration with the scholars and other members of the staff of the institute.

Dey never ceased to take interest in the promotion of scientific research almost to the last day of his life. Just only for a year or so before his death it may be said that he actually retired from active scientific research. In fact, he used to avoid as far as possible all engagements that were likely to distract his attention and interest from science, and seldom cared for the favour or frown from the high quarters, as well as for the lime-light of public applause or the headlines of daily papers. He held aloft the ideal of a true scientist, a real teacher and an ardent educationist.

All jealousies and mean manoeuvring for power and position were hateful to him. Being endowed with noble manners and a righteous nature he always used to resist stoutly any compromise on principle. The foundation of science in India can only be made secure and sound by the silent and dedicated service of devoted teachers and selfless investigators of his type.

In spite of his indifference to name and fame, honours came to Dey unsolicited. His advice and guidance were sought on many occasions both by the public and the State. Dey was a Fellow of the Royal Institute of Chemistry of Great Britain and Ireland, and a member of its Advisory Board. He was a Foundation Fellow of the National Institute of Sciences of India and a Member of its Council for several terms. In 1926 he presided over the chemistry section of the Indian Science Congress Association held in Bombay. He was appointed Chemical Adviser to the Government of Madras and South Indian States for anti-gas warfare during the years 1943-44. Dey served as a member of the Council of Scientific and Industrial Research and as a Chairman of its Chemical Research Committee and of the Heavy Chemicals and Dye-stuff Committee for some time. As a member of the Academic Council and a Fellow of the Senate he rendered conspicuous service to the University of Madras. His service as a member of the Queen Mary's College illustrates his interest in the cause of female education. As Foundation member and President of the Bengal Association, in Madras, and as President of the South Indian Brahmo Samaj, Dey evinced no small interest in social, cultural and religious activities. The Government of West Bengal also sought his wise counsel and guidance by appointing him Chairman of the Secondary Education Committee (1954-55) and a member of the Calcutta University Enquiry Committee.

The Indian Chemical Society honoured him with the highest distinction in their gift by electing him President of the Society for the term 1943-44. He never failed to take keen interest in the activities of the Society and continued as its Vice-President till the last day of his life. He was also elected once in 1949 to deliver the Sir P. C. Rây Memorial lecture, founded by the Society.

Dey married in 1920 Srimati Amiya Ghosh, daughter of the late Gnan Chandra Ghosh of Nagpur. He lost his wife in 1948 and his youngest child, a daughter, in

1942 at a very early age of nine. These two bereavements weighed upon Dey very heavily throughout the rest of his life, but he bore them quite silently and manfully with a spirit of resignation characteristic of the religious trend of his mind. Towards the end of his life he suffered from occasional onsets of bronchial asthma, and it was after a slight indisposition from such an onset that the end came practically without any warning, when he died of heart failure peacefully in sleep at 9 p.m. on the 18th January, 1959, in his own residence at Santhome, Madras. He is survived by his only son and two daughters.

By his passing away the profession of chemistry in India has suffered a severe loss and the country has been deprived of the counsel of a veteran educationist and an able administrator, whose place it will be difficult to fill up for years to come. The Fellows of the Society will miss his wise guidance and his numerous friends and admirers a never-failing and kind-hearted friend.

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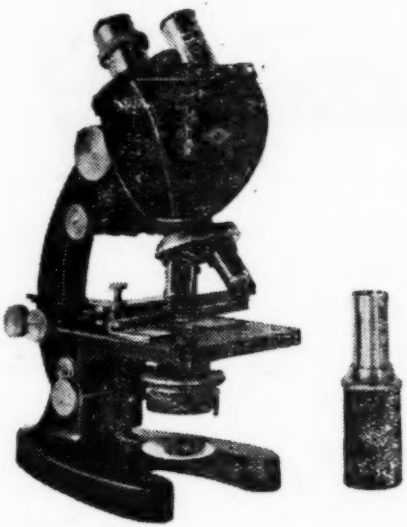

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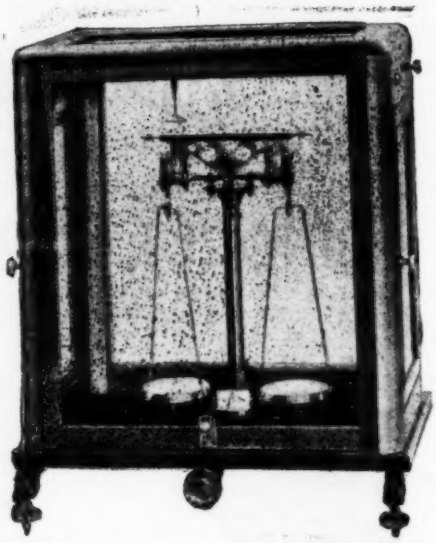

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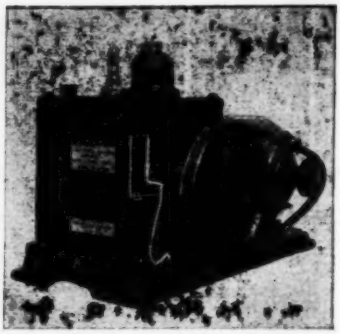

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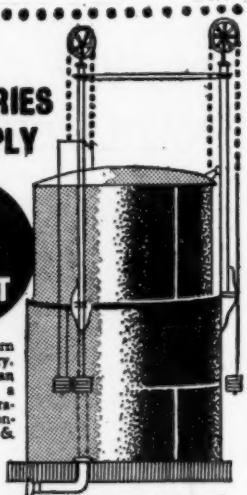

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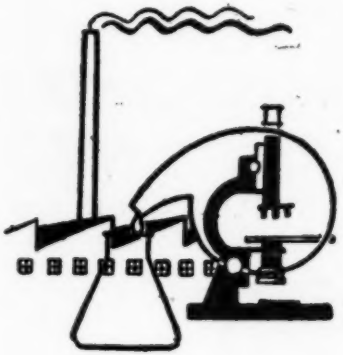

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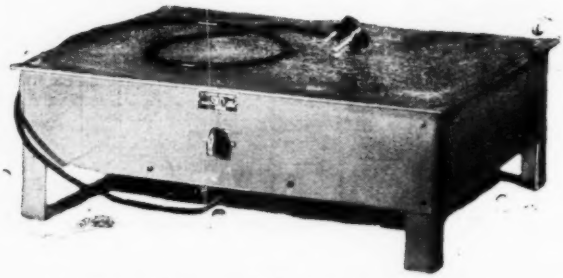

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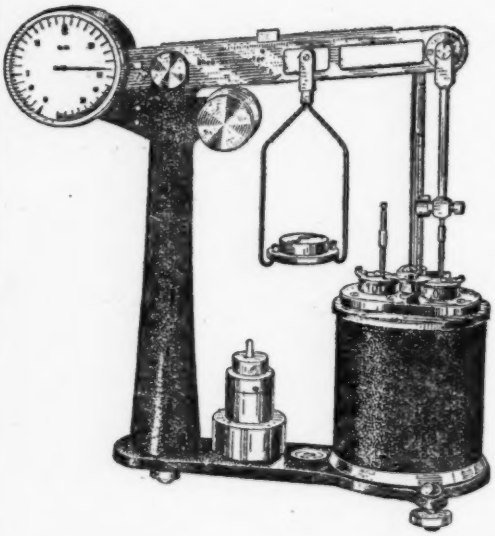

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